Mechanical Characterization of HDPE Polymer Containing Tallow Fatty Acid-coated Precipitated Calcium Carbonate Nanoparticles

Chernet Merkneh Hailemarim

A Thesis Submitted to the Department of Materials Science and Engineering,

School of Mechanical, Chemical and Materials Engineering

Presented in Partial Fulfillment of the Requirement for the Degree of Master's in Materials Science and Engineering

Office of Graduate Studies

Adama Science and Technology University

Jun , 2023

Adama, Ethiopia

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Declaration

I hereby declare that this Master Thesis entitled "Mechanical Characterization of HDPE Polymer Containing Tallow Fatty Acid-coated Precipitated Calcium Carbonate Nanoparticles" is my original work. That is, this thesis has not been presented as part of any other university program to obtain an academic degree, diploma, or certificate. All the sources and materials used in this thesis have been appropriately acknowledged by citing them.

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Recommendation of Advisor

I/we, the advisor(s) of this thesis, hereby certify that I/we have read the revised version of the thesis entitled "Mechanical Characterization of HDPE Polymer Containing Tallow Fatty Acid-coated Precipitated Calcium Carbonate Nanoparticles" prepared under my/our guidance by Chernet Merkneh Hailemarim submitted in partial fulfillment of the requirements for the degree of Masters of Science in Materials Science and Engineering. Therefore, I/we recommend the submission of a revised version of the thesis to the department following the applicable procedures.

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Approval Page

I/we hereby certify that the recommendation and suggestion given by the review Committee are appropriately incorporated into the final thesis entitled "Mechanical Characterization of HDPE Polymer Containing Tallow Fatty Acid-coated Precipitated Calcium Carbonate Nanoparticles" by Chernet Merkneh.

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Approval of Board of Reviewers

We, the undersigned, members of the Board of Examiners of the thesis by Chernet Merkneh Hailemarim have read and evaluated the thesis "Mechanical Characterization of HDPE Polymer Containing Tallow Fatty Acid-coated Precipitated Calcium Carbonate Nanoparticles" and the candidate was evaluated during an open defense session. This is, therefore, to certify that the thesis is accepted for partial fulfillment of the requirement of the degree of Master of Science in Materials Science and Engineering.

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Finally approval and acceptance of the thesis is contingent upon submission of its final copy to the Office of Postgraduate Studies (OPGS) through the Department Graduate Council (DGC) and School Graduate Committee (SGC).

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LIST OF ACRONYMS

ASTM American Society of Testing and Materials

AOAC Association of Analytical Chemists

BET Brunauer-Emmett-teller

EDS Energy-dispersive X-ray spectroscopy

FTIR Fourier Transform Infrared Spectroscopy

GCC Ground Calcium Carbonate

HDPE High Density Poly Ethylene

MTMS Methyltrimethoxysilane

PE Poly Ethylene

PSA Particle Size Analysis

PCC Precipitated Calcium Carbonate

MPCC Mugar Precipitated Calcium Carbonate

MCPCC Mugar Coated Precipitated Calcium Carbonate

PP Polypropylene

PVC Polyvinylchloride

SA Stearic Acid

SEM Scanning Electron Microscope

SBC Sodium Bicarbonate

UTM Universal Testing Machine

TEM Transmission Electron Microscope

VCM Venyl Chloride Monomer

XRD X-ray Diffractometer

ABSTRACT

The use of fillers is a common method for improving the mechanical properties of polymer composites. In this study, we investigate the synthesis and characterization of precipitated calcium carbonate (MPCC) Nano-Powders coated with tallow fatty acid combinations and their application as fillers in high-density polyethylene (HDPE) composites. The coated precipitated calcium carbonate (MCPCC) Nano particles were used as fillers in HDPE composites to enhance the interfacial interaction and mechanical properties. Particle size distribution analysis was performed to ensure uniform dispersion of the coated PCC Nano particles. The weight percentage of MPCC was varied between 0 and 40%, and the best combination of HDPE and MPCC was evaluated to achieve outstanding mechanical qualities. The coated MPCC Nano powder was mixed with virgin HDPE and injection molded to prepare tensile specimens. Thermal analysis, XRD, FTIR, and SEM were used to characterize the HDPE/MPCC and HDPE/MCPCC composites to investigate the dispersion and interfacial interaction between MPCC and the HDPE matrix. The thermal properties of HDPE and its composites were also studied using differential scanning calorimetry (DSC). The mechanical properties of the composites were evaluated, and the optimum weight percent of MPCC in HDPE was found to be 20wt%. A slight decrease in tensile strength occurred after this concentration. A comparison of the tensile strength for similar weight percentages of coated and uncoated MPCC Nano powder showed that tallow-coated MPCC Nano powders increased the tensile strength by 5.5%. Coating the 20wt% MPCC Nano Powder with 10% fatty acids increased the toughness modulus to 33.43 KJ/m3, a significant increase of 14.2% compared to the uncoated 20wt% Nano PCC composite. Overall, the results suggest that tallow-coated MPCC Nano powder is a promising filler for improving the mechanical properties of HDPE composites.

Key words: Coated, Tallow, composite, HDPE, PCC, Fatty acids

CHAPTER ONE

INTRODUCTION

1.1 Background of the study

Composite materials have gained a lot of attention in recent years due to their superior properties compared to traditional materials(Zhu, Abeykoon, and Karim 2021). Polymer composites, in particular, have been widely used in various applications due to their excellent mechanical properties, lightweight, and low cost(Zhu, Abeykoon, and Karim 2021).

High-density polyethylene (HDPE) is a widely used thermoplastic material that offers excellent mechanical properties, such as high strength, stiffness, and toughness(Awan et al. 2021). However, HDPE has a relatively low surface energy, which can lead to poor adhesion and dispersion of fillers, such as precipitated calcium carbonate (PCC), in the polymer matrix(Liu et al. 2002). To address this issue, researchers have investigated the use of surfactants to coat PCC particles and improve their compatibility with HDPE.

The incorporation of fillers into polymer matrices is a common approach to enhance the properties of polymer composites(Risitano, Guglielmino, and Santonocito 2018). Among the available fillers, PCC has attracted significant attention due to its low cost, availability, and unique properties, such as high surface area, small particle size, and high brightness(Lazzeri et al. 2005a). PCC has been used as a filler in various industries, such as paper, paint, plastics, and construction(Aliotta et al. 2019). However, the incorporation of PCC into HDPE can lead to several challenges, such as poor adhesion and dispersion, which can negatively impact the properties of the resulting composites(Ritonga et al. 2022). To overcome these challenges, researchers have investigated various approaches, such as surface modification of PCC particles, the use of coupling agents, and the use of surfactants to coat PCC particles (Durand et al. 2018).The use of surfactants to coat PCC particles has gained significant attention due to its simplicity, effectiveness, and versatility(Abeywardena et al. 2020). Surfactants are amphiphilic molecules that can adsorb at the interface between PCC particles and HDPE and form a stable layer that improves their compatibility(Abeywardena et al. 2021). Several types of surfactants have been investigated for coating PCC particles, including fatty acids, sodium stearate, sodium dodecyl sulfate (SDS), and Tween 80(Kiss, Fekete, and Pukánszky 2007).

The coating process for PCC particles typically involves mixing the surfactant with the PCC in a solvent, followed by drying and milling to obtain coated PCC particles(Papirer, Schultz, and Turchi 1984). The choice of solvent can affect the coating process and the resulting properties of the coated PCC particles(Patti et al. 2021). The drying temperature and time can also affect the coating process and the properties of the coated PCC particles(Liang et al. 2018).
Coating PCC particles with surfactants has been shown to improve the mechanical properties, rheological behavior, morphology, and thermal stability of HDPE/PCC composites(Fekete et al. 1990). For instance, coating PCC with stearic acid, sodium stearate, or Tween 80 has been shown to improve the tensile strength and Young's modulus of HDPE/PCC composites, reduce the viscosity of the polymer melt, and enhance the dispersion of PCC particles in the polymer matrix(Ritonga et al. 2022). Coating PCC particles with surfactants is a promising method for improving the compatibility and performance of HDPE/PCC composites, which have potential applications in various industries, including packaging, construction, and automotive (Jimoh et al. 2018c). However, further research is necessary to optimize the coating process and evaluate the long-term performance of HDPE/PCC composites coated with surfactants. The objectives of this thesis are to investigate the effectiveness of a specific surfactant for coating PCC particles in HDPE compounding and to evaluate the properties of the resulting HDPE/PCC composites. The thesis will systematically examine the impact of surfactant type and processing conditions on the morphology, mechanical properties, and thermal stability of HDPE/PCC composites. Additionally, the thesis will compare the performance of surfactant-coated PCC with that of uncoated PCC and other commonly used fillers in HDPE composites (Jimoh et al. 2018c).

In summary, the use of surfactants to coat PCC particles in HDPE compounding is a promising research direction that can contribute to the development of high-performance polymer composites. This thesis aims to provide a comprehensive understanding of the effect of natural surfactant on the properties of HDPE/PCC composites and to develop coating process that can enhance their performance. To achieve improved properties in polymer composites, have to use such additives as pigments, inhibitors, antioxidants, plasticizers and other compounds(Rothon 2017). Materials including the inorganic particles (oxides, nitrides, carbides, silicates etc.) are introduced to the polymer matrixes. Incompatibility of these inorganic and organic components main problem has to be solved(S. Sun et al. 2019). One of

the most progressive trends of filled materials making, where the filler defines synthesis kinetics, structure and properties of final product and at the same time performs the role of catalyst, is polymer's synthesis in the presence of inorganic fillers(Ippolito et al. 2020). Saturated complex polyethers, particular polybutylenetherephtalate (PBT), are used as enginiring thermoplasts, having a good thermos and wear stability, excellent performance(Donate-Robles, Liauw, and Martín-Martínez 2014). These properties allow also to apply them as a matrix material for polymer composites.

This research broadly relates to treated filler materials, more particularly, to surface-treated calcium carbonate, and still more particularly to calcium carbonate surface-treated with a high molecular weight saturated fatty acid for use as filler in HDPE and PP to improve the compounding adhesion and mechanical properties simultaneously extending the bulk , reducing the cost of polymer products.

1.2 Statement of the Problem

The utilization of high-density polyethylene (HDPE) products is rapidly expanding in Ethiopia due to the growing demand for cost-effective and durable plastic items across various industries(KE 2016). However, the reliance on imported filler materials can hinder the technical application of HDPE products and lead to environmental sustainability issues (Byrne et al. 2009). Hence, there is a pressing need to develop locally sourced and affordable fillers that can enhance the quality of HDPE products while reducing dependence on imported materials.

One promising filler material is precipitated calcium carbonate (PCC) nanoparticles, which possess favorable characteristics such as low cost, abundance, and distinctive properties. Nonetheless, their hydrophilic nature poses a compatibility challenge with hydrophobic polymers like HDPE, limiting their effective use in HDPE products (Global and Outlook 2020). Therefore, the objective of this research is to assess the organic modification, specifically the tallow surface treatment of Mugar PCC nanoparticles, as a means of improving their compatibility with HDPE. The study aims to enhance the mechanical and thermal qualities of HDPE products.

Previous studies have suggested the use of specific fatty acid surface treatments to enhance compatibility in composite materials (Lazzeri et al. 2005b). However, the impact of tallow fatty

acid combinations on the properties of HDPE products remains unclear. The challenge lies in identifying a suitable surface agent that can reduce the surface tension between inorganic particles and the polymer matrix, ensuring good dispersion. Additionally, the agent should easily separate from the interphase region between the filler and the polymer, facilitating debonding and promoting the formation of micro voids.

Consequently, this research aims to investigate the potential of PCC nanoparticles as a filler material in HDPE products, incorporating tallow fatty acid combinations as a surface treatment. The study will comprehensively evaluate the mechanical, thermal, and morphological properties of HDPE/PCC composites with and without tallow surface treatment. By doing so, it will determine the optimal conditions for achieving improved compatibility and enhanced properties in the HDPE products.

1.3 Objectives of the study

1.3.1 General objective

The general objective of this research is to develop mechanically stable composite Materials based on HDPE polymer containing Mugar Precipitated Calcium Carbonate Nanoparticles Coated with Tallow Fatty Acid

1.3.2. Specific Objectives

- To synthesize and characterize PCC nanoparticles using solution method
- To investigate the effect of surface modification of PCC nanoparticles on their compatibility with HDPE.
- To evaluate the effect of tallow surface treatment on thermal properties of HDPE Nano PCC composites
- To investigate the mechanical and thermal properties of HDPE PCC composites with and without organic modification; tallow surface treatment, and to determine the optimal conditions for achieving improved properties.

1.4 Significance of the study

- The study will contribute to the development of sustainable and cost-effective filler materials for the polymer industry, by investigating the potential of PCC nanoparticles

as a locally-sourced and low-cost alternative to imported fillers. This can potentially reduce the cost of production and increase the competitiveness of the Ethiopian Polymer Industry, while also reducing the environmental impact of the industry.

- The research will look at the influence of tallow surface treatment on the compatibility and characteristics of HDPE/PCC composites, with an emphasis on improving mechanical and thermal properties. This may result in the development of HDPE products with increased performance and functionality that can be employed in a variety of applications. The study focuses on the potential replacement of imported fillers in the Ethiopian Polymer Industry, which can promote local economic development and reduce the dependence on foreign imports. This can lead to the creation of local jobs and the development of local expertise in the field of polymer science and technology.
- The study will contribute to the growing body of research on the development of sustainable and cost-effective filler materials for the polymer industry, with a focus on the optimization of organic modification and surface treatment techniques. This can provide insights into the potential of PCC nanoparticles as a filler material for HDPE products, and the effectiveness of organic modification and tallow surface treatment in enhancing their compatibility and properties.

1.5 Scope of the Study

The scope of this study is to investigate the potential of Mugar precipitated calcium carbonate (PCC) nanoparticles as a sustainable and cost-effective filler material in high-density polyethylene (HDPE) products, with the presence of tallow surface treatment, as a potential replacement for imported fillers in the Ethiopian Polymer Industry. The study will utilize a solution approach for PCC synthesis, and will focus on the characterization of the synthesized nanoparticles thermal stability, functional group evidencing using FTIR and morphological studies. The mechanical properties of HDPE/Mugar PCC composites were evaluated using tensile testing, and the impact of organic modification and tallow surface treatment on the compatibility and properties of the composites were investigated. The research provides insights into the potential of Mugar PCC nanoparticles as a filler material for HDPE products, and the effectiveness of organic modification which is tallow surface treatment in enhancing their compatibility and properties, with a focus on the optimization of synthesis and characterization techniques.

1.6 Limitation of the Study

In this research, there were several limitations encountered. Firstly, the utilization of old, vertically-oriented, and poorly maintained injection molding equipment posed constraints on the study. The outdated and unmaintained nature of the machinery could have affected the consistency and precision of the injection molding process, potentially introducing variability in the produced samples and impacting the accuracy of the mechanical characterization. It is important to acknowledge these limitations when interpreting the results and considering their generalizability to other injection molding setups. Future studies would benefit from using modern and well-maintained injection molding machinery to improve the reproducibility and reliability of the experimental outcomes. Additionally, other limitations include material supply constraints, which affected the availability and consistency of the HDPE polymer and tallow fatty acid-coated PCC nanoparticles, potentially introducing variations in the results. The research primarily focused on the mechanical characterization of the HDPE polymer, with limited exploration of the calcium ion supply due to the absence of the carbonation method because of the cost and complexity. Addressing these limitations in future research would provide a more comprehensive understanding of the mechanical characterization and potential applications of HDPE polymer containing tallow fatty acid-coated PCC nanoparticles.

1.7 Organization of the thesis

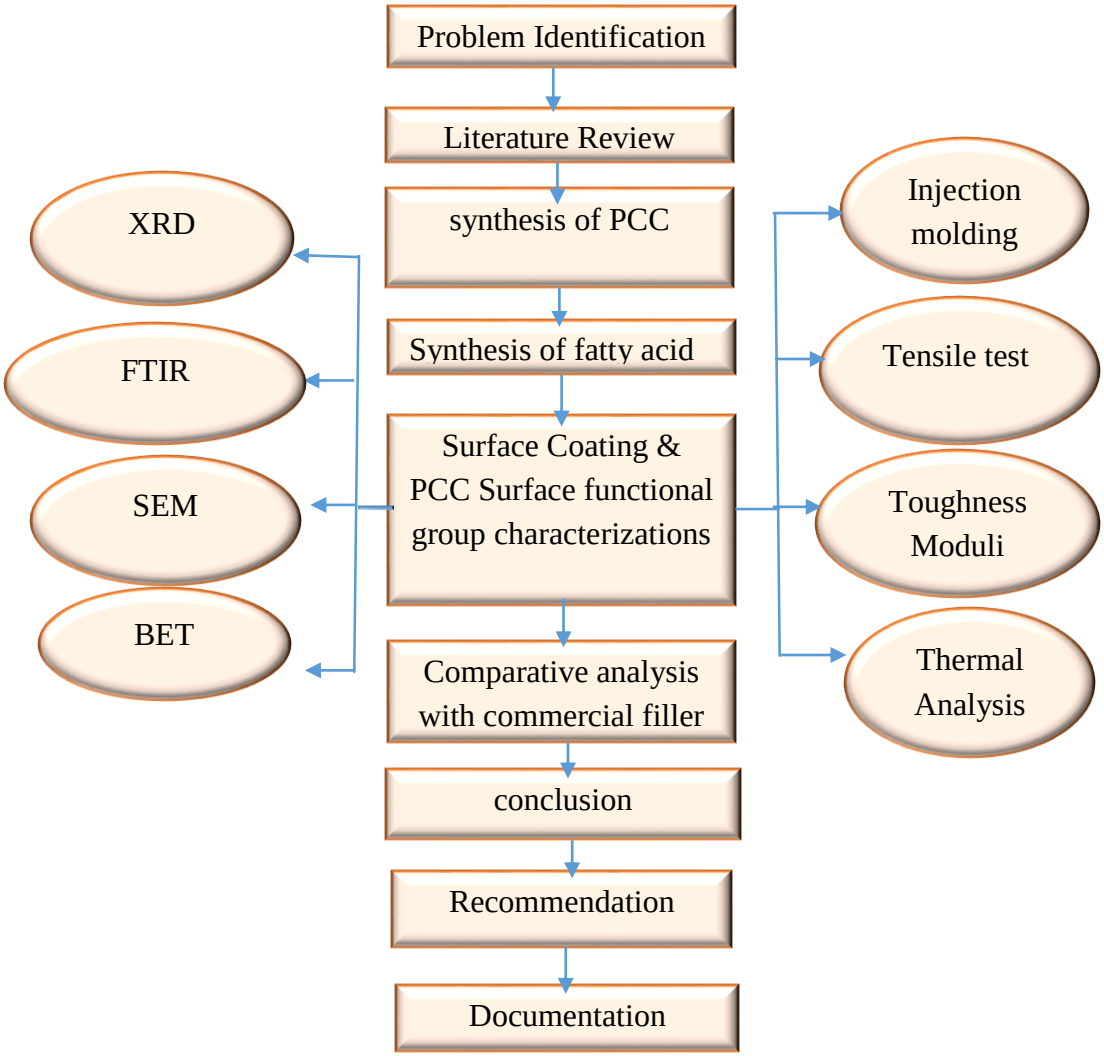

Figure 1.Thesis organization

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Fillers are solid materials that are added to a polymer matrix to improve the properties of the resulting composite(Semakina et al. 2015). Fillers can be either organic or inorganic materials, and they are typically added to the polymer matrix at low concentrations to reduce the cost of the composite(Imai 2021). Fillers can improve the mechanical, thermal, and barrier properties of the composite, while also reducing its coefficient of thermal expansion and water absorption(Awan et al. 2021). Inorganic fillers, such as silica, alumina, calcium carbonate, and talc, are commonly used in polymer composites due to their high strength, stiffness, and thermal stability(Imai 2021). Among the inorganic fillers, Precipitated Calcium Carbonate (PCC) is a popular choice due to its high brightness, low oil absorption, and low cost compared to other fillers(Zhu, Abeykoon, and Karim 2021). PCC is produced by the reaction of calcium hydroxide with carbon dioxide, resulting in the formation of calcium carbonate particles(Thenepalli et al. 2015). Organic fillers, such as wood flour, cellulose, and lignin, are also used in polymer composites. Organic fillers can improve the mechanical properties of the composite while also providing a natural appearance(Elkhouly et al. 2022). However, organic fillers are typically more expensive than inorganic fillers and may have limitations in terms of durability and thermal stability(Jimoh et al. 2018a).

2.2 Precipitated Calcium Carbonate as a filler

PCC is a widely used filler in polymer composites due to its low cost, availability, and unique properties, such as high surface area, small particle size, and high brightness. The addition of PCC to HDPE can improve the stiffness and strength of the composite, up to a certain content, beyond which the properties can deteriorate due to the agglomeration of PCC particles. Several studies have investigated the effect of PCC content and particle size on the properties of HDPE/PCC composites. For instance,(Zebarjad et al. 2006) studied the effect of PCC content (0-30 wt%) on the mechanical properties of HDPE/PCC composites. The results showed that the tensile strength and elongation at break of the composites increased with increasing PCC

content up to a certain content (10 wt%), beyond which the properties decreased due to the agglomeration of PCC particles. The compressive strength and modulus of the composites showed a similar trend. Similarly, (Huang et al. 2013)investigated the effect of PCC content (0-30 wt%) and particle size (1 μm and 5 μm) on the mechanical properties of HDPE/PCC composites. The results showed that the tensile strength and Young's modulus of the composites increased with increasing PCC content and decreased with increasing PCC particle size. The impact strength and elongation at break of the composites decreased with increasing PCC content and particle size.

2.2.1 Surface Modification of PCC

The poor adhesion and dispersion of PCC particles in HDPE can be improved by surface modification of PCC particles(Lam et al. 2009). Several approaches have been investigated to modify the surface of PCC particles, including silane coupling agents, fatty acids, and cationic surfactants. For instance, (González et al. 2002)investigated the effect of silane coupling agents on the mechanical properties of HDPE/PCC composites. The results showed that the addition of silane coupling agents improved the interfacial adhesion between PCC and HDPE, leading to improvements in the mechanical properties of the composite. Similarly, (Fekete et al. 1990)investigated the effect of stearic acid on the mechanical properties of HDPE/PCC composites. The results showed that the addition of stearic acid improved the dispersion of PCC particles in the polymer matrix, as well as enhanced the interfacial adhesion between PCC and HDPE. The use of cationic surfactants, such as cetyltrimethylammonium bromide (CTAB), has also been investigated to improve the dispersion of PCC particles in HDPE(Kanoje, Patel, and Kuperkar 2017). For instance, Li et al. (2017) investigated the effect of CTAB on the mechanical properties of HDPE/PCC composites. The results showed that the addition of CTAB improved the dispersion of PCC particles in the polymer matrix, leading to improvements in the mechanical properties of the composite.Table.2 mentions many literatures with PCC and its surface treatment with mechanical properties . Reactive surface modifiers can serve as coupling agents between the filler and the polymer. Surface modification frequently enhances the production of fillers, the processing of composites, and the attributes of composites. They frequently do not react with the polymer but rather change energies or interactions to improve compatibility.

Surface moderators are employed as milling aids, to enhance filtration, and to lessen the formation of hardness after drying(C. quan Li et al. 2021). Because it offers a good match for the surface of calcite, stearic acid is the most frequently utilized saturated fatty acid for the surface modification of calcium carbonate(Nguyen et al. 2020a). However, the majority of commercial grades of stearic acid utilized in pre-coating fillers are complex mixes with low levels of stearic acid(Coons 1950).

2.2.2 Coupling Agents and Surfactants

The use of coupling agents and surfactants is another approach to improve the compatibility and dispersion of PCC particles in HDPE. Coupling agents, such as maleic anhydride grafted HDPE (MAPE), can improve the adhesion between PCC and HDPE by forming covalent bonds between the filler and the polymer matrix(Husseinsyah, Azmin, and Ismail 2013). (Rothon 2017)investigated the effect of maleic anhydride grafted polyethylene (MAPE) and stearic acid on the mechanical properties of HDPE/PCC composites. The results showed that the addition of both MAPE and stearic acid improved the tensile strength and Young's modulus of the composites, as wellas enhanced the dispersion of PCC particles in the polymer matrix.

Surfactants, such as Tween 80 and stearic acid, can also improve the dispersion of PCC particles in HDPE(Shi, Rosa, and Lazzeri 2010). For instance, Wang et al. (2021) investigated the effect of Tween 80 and stearic acid on the mechanical properties of HDPE/PCC composites. The results showed that the addition of both surfactants improved the tensile strength and elongation at break of the composites, as well as enhanced the dispersion of PCC particles in the polymer matrix. The use of surfactants can also improve the compatibility between the filler and the polymer matrix by reducing the interfacial tension between them. The creation of a mono-layer covering is the most crucial theoretical idea. The concentration of stearic acid is calculated (C_{100}) which required to completely bond the calcium carbonate Surface without dissolving using a method known as the "dissolution Method." (Gypsum et al. 2018)

The Cmax is the maximum amount of stearic acid concentration that can attach to the surface. The dissolving was used to determine C_{100} and Cmax(Singh et al. 2008),(Teixeira et al. 2006). A strong attachment of the fatty acid to the filler surface must be obtained. It is preferable to generate a partial salt with the metal cation of the filler rather than a whole salt.

The metal ion will no longer be a part of the filler structure and can be easily removed from the surface if a complete salt is produced. Ionic calcium carbonate combines with stearic acid to generate a basic alternative on the surface.

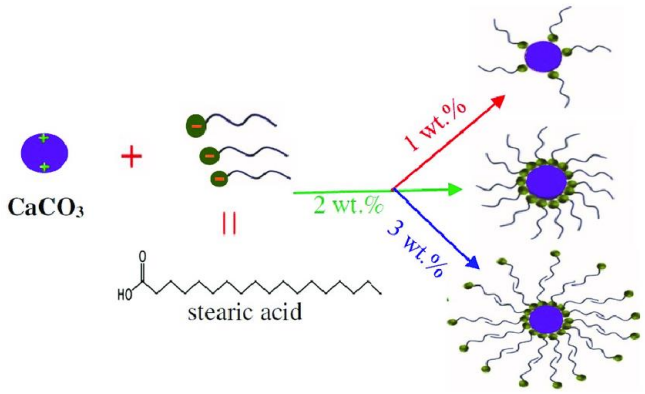

Figure 2.Attachment of stearic acid molecules on to the calcium(Chengyu Wang et al. 2010)

Each surface Ca^{2+} ion can only accept one stearate ion, and they are vertically aligned to the surface as depicted in the figure below. According to reports, a perpendicularly orientated stearate molecule has an area of about 21 Angstroms(Nguyen et al. 2020b). Fatty acids can absorb in both the net and the perpendicular plane to the surface, which can alter the theoretical coating monolayer as shown in Figure 2. Below.

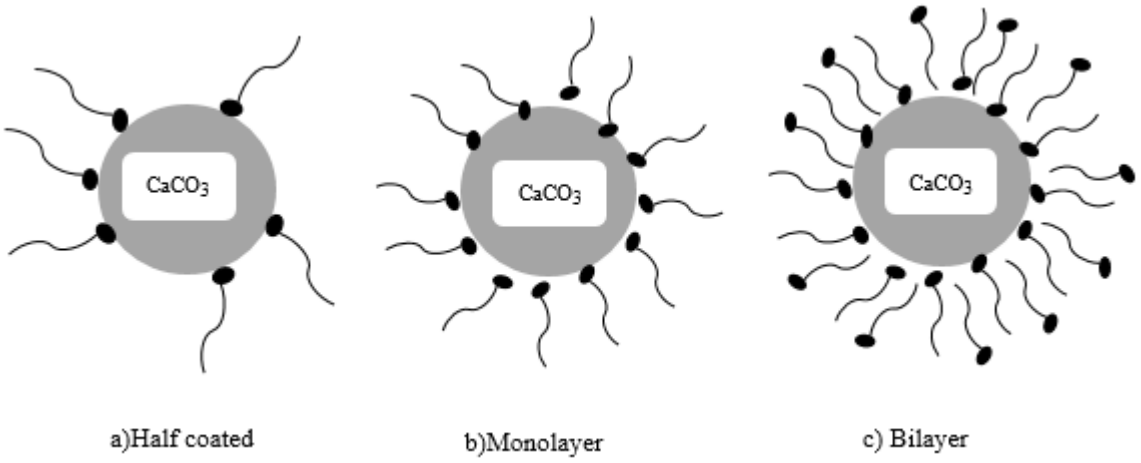

Figure 3.Fatty acids coatings a) Half coated b)Monolayers c)Bilayers (Kanoje, Patel, and Kuperkar 2017)

According to (Filippova et al. 2018); It is also possible for a bulk reaction to take place when fatty acids are utilized with fillers rather than the anticipated surface reaction, which would result in the creation of discrete fatty acid salts, as shown in the figure below. This is a negative consequence, so the coating procedure must be carefully managed to reduce it. In general, there are three types of surfactants: cationic (like quaternary amine salts), anionic (like stearic acid, salt), and nonionic (like fatty alcohol polyoxyethylene ether). Fatty acid (salt) is the most often used surfactant out of all of them because, during the in-situ production and modification of $CaCO_3$ using sodium stearate as the modifier, the molar ratio of the calcium ion to the sodium stearate was two(DING et al. 2007)

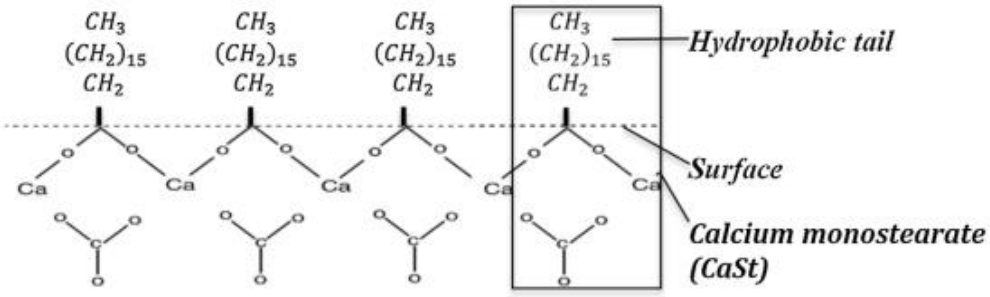

Figure 4.Stearic acid chemical structure and principle of $CaCO_3$ monolayer surface treatment with stearic acid(Cao et al. 2016).

(Pradittham et al. 2014a) prepared the isotactic polypropylene (PP) composite films filled with SA modified $CaCO_3$ particles which showed great application potential in microwave packaging. In comparison to pure PP films and composite films containing unaltered $CaCO_3$ particles, the mechanical and thermal properties of the composite films following microwave irradiation were significantly enhanced(Pradittham et al. 2014b). Fatty acids with various carbon chain lengths were also utilized in addition to stearic acid to alter $CaCO_3$. The results also revealed that the changed $CaCO_3$ samples water contact angles rose as the length of the carbon chain increased, indicating that the samples' hydrophobicity increased as a result. The longer the carbon chain, the more compatible the modified $CaCO_3$ samples were with the polymer. Palmitic acid, another typical fatty acid, has been demonstrated to be effective for the modification of $CaCO_3$ as well(Chenglong Wang et al. 2021) . Carboxyl groups in oleic acid molecules could react with hydroxyl groups on the surface of $CaCO_3$ to form chemical bonds, which resulted in the coating of oleic acid on the $CaCO_3$ surface (Osman and Suter 2002a).

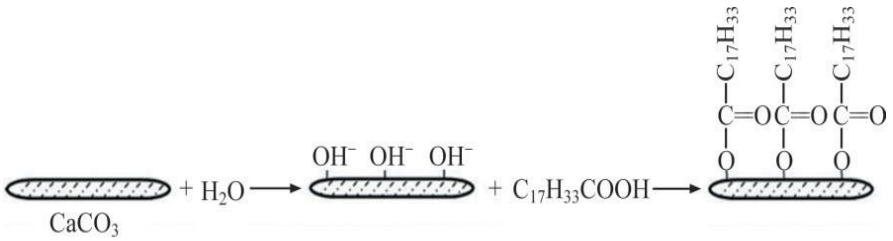

Figure 5.Ihe Interaction mechanism between CaCO3 and oleic acid molecules(RITONGA ET AL. 2022)

2.3 Influence of Surface modification on PCC

Before filling the $CaCO_3$ powder into polymers to prepare the composite materials, it is necessary to modify the $CaCO_3$ powder to enhance the interfacial interaction between $CaCO_3$ powder and the matrix. As for the $CaCO_3$ powder modification, modifier type, modifier dosage, modification time, modification temperature, etc. could affect the modification effect. In comparison with modification time and modification temperature, modifier type and modifier dosage are relatively more significant influencing factors(Rahmani, Ghasemi, and Payganeh 2014).

During the past years, various types of modifiers had been used for $CaCO_3$ modification, which exhibited different modification effect. The measurement of water contact angle is one effective way to characterize the modification effect, indicating the hydrophobicity of the modified $CaCO_3$ particles. (Kandirmaz et al. 2020) reported the in-situ modification of $CaCO_3$ with calcium stearate, and it was concluded that when the usage amount of calcium stearate was 5.5 wt% , the water contact angle of the modified sample reached 107.8° and the activation index was 99.8%, while that of the unmodified sample was 9.9° and 0.0%, respectively(Meng et al. 2020). When the $CaCO_3$ powder was modified with the anionic fluorinated surfactant (Zonyl TBS), it was found that the highest water contact angle of the modified $CaCO_3$ powder reached 115.1° with the modifier dosage of 0.38% (Deshmukh et al. 2010). Moreover, the water contact angle can reach to 99.2° , 103° and 134° when the $CaCO3$ powder was modified with silane coupling agent methyltrimethoxysilane (MTMS), 3-methacryloxypropyltrimethoxysilane (KH570) and aluminate coupling agent, respectively (He et al. 2011; Robaidi et al. 2011). When the modified $CaCO_3$ is filled into polymer matrix to prepare composite materials, the mechanical properties of the composite materials can be influenced by the modifier types and polymer matrix.

The literature review reveals various studies on the incorporation of modifiers in precipitated calcium carbonate (PCC)-based polymer composites. (Barkoula et al. 2008)investigated the use of stearic acid as a modifier in polypropylene (PP) composites with PCC. They observed an improvement in the elastic modulus while the tensile strength and elongation at break remained unchanged. (Xie et al. 2023)studied high-density polyethylene (HDPE) composites with stearic acid-modified PCC and found an enhancement in the tensile strength and elastic modulus, but no effect on elongation at break.

In the case of polyethylene (PE) composites, (Qing Li et al. 2002)utilized sodium stearate as a modifier. They reported an increase in the tensile strength, but no significant changes in elongation at break. Yang et al. (2010) investigated ethylene-octene copolymer composites with a silane coupling agent (VTMS) as a modifier. The incorporation of VTMS resulted in improvements in both tensile strength and elongation at break, as well as an increase in the elastic modulus. (Abd El-Hakim et al. 2019) studied chlorinated polyvinyl composites with stearic acid as the modifier. They observed an enhancement in the tensile strength, but no significant change in elongation at break. (Legato 2020)explored epoxy composites with a silane coupling agent (KH550), which led to improvements in tensile strength, elongation at break, and the elastic modulus. (Pechyen and Ummartyotin 2017) investigated isotactic polypropylene composites with stearic acid as a modifier. The incorporation of stearic acid resulted in an improvement in the tensile strength and elastic modulus, but a decrease in elongation at break (Ippolito et al. 2020) studied polydimethylsiloxane composites with stearic acid as the modifier. They observed significant improvements in both tensile strength and elongation at break, as well as an increase in the elastic modulus.

González et al. (2002) and Zhang et al. (n.d.) investigated polyvinyl chloride (PVC) composites with a titanate coupling agent as a modifier. They reported an enhancement in tensile strength and elastic modulus, but a decrease in elongation at break. Pradittham et al. (2014a) studied PP composites with palmitic acid as the modifier, which resulted in an improvement in tensile strength and elastic modulus, but a decrease in elongation at break.

Overall, the literature suggests that the addition of modifiers, such as stearic acid, silane coupling agents, and titanate coupling agents, can generally lead to improvements in mechanical properties such as tensile strength and elastic modulus. However, the effect on

elongation at break varies, with some modifiers causing a decrease or no significant change. It is important to consider these findings when selecting a suitable modifier for PCC-based polymer composites, as the desired mechanical property improvements may vary depending on the specific application requirements.

The amount of the modifier is also an important factor in $CaCO_3$ modification(Bai and Li 2023). Monolayer coating, in which each modifier molecule is coupled to calcium ions and directed vertically to the surface of the particles, is the best coating method for $CaCO_3$ particle modification(Osman and Suter 2002b). Based on the surface area and crystal structure of the $CaCO_3$ particles, this can be estimated. However, due to the physical and chemical adsorption that occurred in the coating layer throughout the present modification process, whether dry modification, wet modification, or complicated modification, the perfect CaCO3 coating cannot be guaranteed (Rothon 2017).

$CaCO_3$ has a poor modification impact when the amount of modifier used is insufficient, resulting in particle aggregation and uneven dispersion in the polymer matrix. The additional modifier, on the other hand, causes a partial or complete bilayer, or even a multilayer, of modifier to form on the surface of the $CaCO_3$ particles(Rahmani, Ghasemi, and Payganeh 2014), which reduces the modification effect to some extent, further deteriorating the mechanical properties of the composite material. According to the relevant study, in the presence of a high concentration of modifier, the surface properties of $CaCO_3$ changed from hydrophobic to hydrophilic due to the formation of the bilayer or multilayer structure of modifier. $CaCO_3$'s hydrophobicity could be improved by increasing the modification dosage below the required monolayer coating dosage(Osman and Suter 2002a). An anionic surfactant, alkyl benzene sulfonic acid, is a good example of how the modifier dosage clearly affected the modified $CaCO_3$'s contact angle with water(Hydrophobic Tail n.d.). The angle of contact of the modifier Because alkyl benzene sulfonic acid formed a bilayer structure, $CaCO_3$ increased with the amount of modifier and then began to decrease once it reached its maximum value.

2.4 Processing Parameters

The processing parameters, such as the mixing method, mixing time, and processing temperature, can also affect the properties of HDPE/PCC composites(Ramesh, Rajeshkumar,

and Balaji 2021). The mixing method can affect the dispersion of PCC particles in the polymer matrix, with a twin-screw extruder being more effective than a single-screw extruder. For instance, (Hongzhen, Keyan, and Weiming 2017) investigated the effect of processing parameters on the mechanical properties of HDPE/PCC composites. The results showed that the use of a twin-screw extruder led to better dispersion of PCC particles in the polymer matrix compared to a single-screw extruder. The mixing time also affected the mechanical properties, with longer mixing times leading to better dispersion of PCC particles and improved mechanical properties. The processing temperature can also affect the mechanical properties of HDPE/PCC composites, with higher temperatures leading to better dispersion of PCC particles and improved mechanical properties.

2.5 PCC Synthesis Processes

The solution-based synthesis of Nano-PCC involves modifying the traditional PCC synthesis process to control the size and morphology of the particles. The synthesis process generally involves two stages: nucleation and crystal growth(Jimoh et al. 2018b). In the nucleation stage, small clusters of calcium carbonate particles are formed through the reaction of calcium and carbonate ions in the reaction mixture. The nucleation stage can be controlled by adjusting the concentration of calcium and carbonate ions, pH, and temperature of the reaction mixture(Kandirmaz et al. 2020). In the crystal growth stage, the nucleated particles grow into larger, well-defined crystals. The crystal growth stage can be controlled by adjusting the reaction time, temperature, and agitation rate of the reaction mixture. To synthesize Nano-PCC, the nucleation and crystal growth stages are carefully controlled to promote the formation of smaller and more uniform particles. This can be achieved by adjusting the concentration of calcium and carbonate ions, pH, temperature, and agitation rate of the reaction mixture. In addition, surfactants or other organic molecules can be used to stabilize the nucleation and growth of the PCC particles, resulting in smaller and more uniform particles(Kanoje, Patel, and Kuperkar 2017). The solution-based method for synthesizing Nano-PCC can be performed using different methods, including the lime-soda process, the double decomposition method, and the use of precipitation from an aqueous solution. Each method has its advantages and disadvantages, depending on the desired properties of the resulting Nano-PCC(Kitamura et al. 2002).

Overall, the synthesis of Nano-PCC involves carefully controlling the reaction conditions to produce particles with the desired morphology, size, and purity. The selection of the synthesis method depends on the desired properties of the Nano-PCC and the specific application.

2.6 Polymorphs of PCC

There are three possible spatial configurations of calcium and carbonate ions that make up calcium carbonate(J. Sun, Wang, and Zhao 2017). Calcite, aragonite, and vaterite are the three polymorphs of calcium carbonate . All of these polymorphs can be created using procedures that result in synthetic precipitated calcium carbonate, or PCC, and are seen in nature(Chen and Xiang 2009). The main and most common one which is emphasized in our research is Calcite. Calcite has a rhombohedral crystal structure and is widely used as a filler in the plastics industry due to its high brightness, low oil absorption, and low cost compared to other fillers(García Carmona, Gómez Morales, and Rodríguez Clemente 2003). It is also used in the paper industry and other applications where high whiteness and brightness are desired(Erdogan and Eken 2017). Aragonite has a needle-like crystal structure and is thermodynamically less stable than calcite but more stable than vaterite(Sindhu et al. 2004). Aragonite is commonly used in applications such as paper and paint due to its high brightness and whiteness(Per, Vueak, and Krstulovib 1996). Vaterite has a spherical crystal structure and is the least stable of the three polymorphs. It is less commonly used as a filler due to its lower stability and tendency to transform into other polymorphs(Chen and Xiang 2009). However, it is used in some applications such as food, pharmaceuticals, and cosmetics due to its high surface area and reactivity(J. Seo et al. 2014). Understanding the properties and differences between the polymorphs of PCC is important for optimizing their use in various industrial applications.

2.7 Ethiopian Mugar Limestone as a Source of PCC

There are Over 100,000 square kilometer of carbonate rocks are exposed in Ethiopia but very little is known about the active mining site within the deposit . Mugar is one those mining sites (Of et al. 2018). The limestone deposits vary from pure limestone through magnesium limestone to dolomites, according to Gumerov and Aklilu Asefa (1981) and Tibebu Mengiste et al., (1993), as mentioned in Solomon Tadesse et al., (2003). Ethiopia has enormous, unestimated quantities of limestone. The limestone sites mainly reserves for cement manufacture in the Mugher valley and Dire Dawa are estimated to be more than 100 and 4.6

million tones, respectively(Tadesse, Milesi, and Deschamps 2003). In this research, Mugar limestone is considered as a potential source of raw material for the production of high-quality PCC. The Muger limestone deposit is one of Ethiopia's largest and has been intensively mined for several decades and it is of good quality, with characteristics such as homogeneity, durability, and low impurity concentration(Of et al. 2018). The quality of the limestone used in the production of PCC can affect the properties of the resulting PCC particles. The origin country of the limestone can also affect the quality of the resulting PCC particles(Teir et al. 2016). The quality of the limestone can vary depending on its geographical location, geological formation, and mineral composition(Elgohary et al. 2022). For instance, limestone from different regions in China has been shown to have different mineral compositions and impurity levels, which can affect the properties of the resulting PCC particles(Yan et al. 2022). In general, high-purity limestone with low impurities such as silica, iron, and aluminum is preferred for the production of high-quality PCC(Owais et al. 2019). Muger limestone has aided the development of Ethiopia's building sector and contributed to the country's economic progress. Below are other different sites of limestone deposits of Ethiopia.

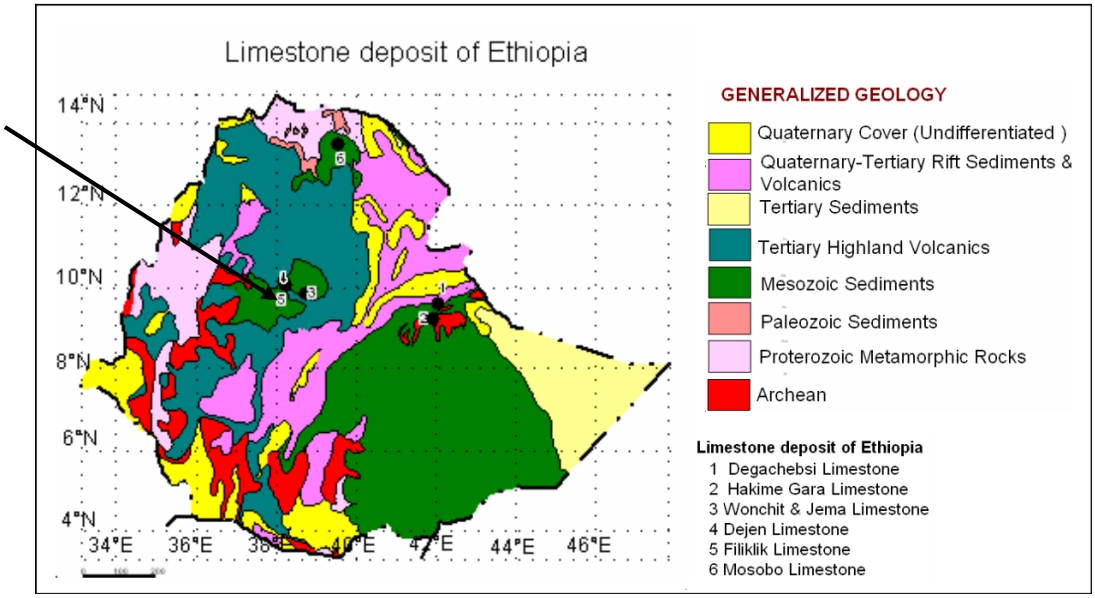

Figure 6.Geological and known limestone deposits in Ethiopia(Tadesse, Milesi, and Deschamps 2003)

Generally, The development of the nation's limestone resources supposed to help the economy of the nation grow, save foreign money, create jobs, and advance the manufacturing, building, and agricultural industries specially in polymer production industries hasn't been utilized as the availability. Table 1 . puts in place the imports of calcium carbonate products to Ethiopia.

Table 1.Imports of calcium carbonate 2000-2005(Morgan and Survey 2022).

Calcium Carbonate						
Year	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**
Tons Us dollar Us-per ton		879 176,685 201	1,011 193,197 191	1,605 250,254 218		
Chalk						
Tons Us-dollar Us-per ton Origin	35 7528 213 Auk France	<1 31 4477	39 9360 240 Netherlands Taiwan	22 7370 330 Netherlands	26 6876 264 France Pakistan	17 1132 65 China

2.8 Research Gap

Previous studies have investigated the use of precipitated calcium carbonate (PCC) as a filler in high-density polyethylene (HDPE); however, there is a research gap in exploring suitable and efficient surface agents that can reduce the surface tension between inorganic particles and the polymer matrix, allowing for good dispersion while also being able to disentangle quickly from the interphase region between the filler and the polymer. This characteristic allows for easy deboning and promotes thermal as well as mechanical behavior, which has not been fully explored in previous researches. Specifically, no research has been conducted to find adequate

surface modifier as tallow fatty acid combination coating of Nano PCC particles to improve their compatibility with HDPE matrices. Additionally, the geographical location of minerals can have an impact on their products, and specifically, the origin of limestone can be considered as one of the research variables in the production of PCC. Despite this, there has been a lack of research on Ethiopian high-quality limestone for PCC production.

To address these research gaps, this study aims to investigate suitable surface agent for coating PCC Nano particles to improve their compatibility with HDPE matrices, allowing for good dispersion and easy debonding. Additionally, this study aims to analyze the particle size distribution to optimize the compatibility and mechanical properties of HDPE/PCC composites. Moreover, this study aims to evaluate local minerals for PCC production, specifically Ethiopian high-quality limestone. By addressing these research gaps, this study will provide valuable insights into the optimization of material design and processing parameters for achieving the desired properties of polymer composites.

CHAPTER THREE

MATERIALS METHODS AND CHARACTERIZATIONS

3.1 Chemicals

In this research work, raw materials of different chemicals, which were utilized for the synthesis of Precipitated Calcium Carbonate and polymer blending are: Commercial PCC powders, HDPE pellets, Industrial Coated PCC filler, Sodium Carbonate, Calcium chloride, Hydrochloric acid ,n-heptane for fat dissolving and coating. Additionally distilled water and ethanol are used for all syntheses and treatment processes (as a solvent for dissolving chemicals and for washing purposes in centrifuging processes). All chemicals (precursors) and precipitating agents were commercially purchased with analytical purity ≥ 99% which are used to prepare a coated precipitated calcium carbonate nanoparticle as a filler master batch for HDPE .

The sequential procedures used in this research are as follows:

3.2 Preparation of CaO(Quicklime)

Chunks of limestone were crushed into a manageable size range of 10–20 mm diameter before calcined in a muffle furnace at an optimum disassociation temperature and resident time. High reactive and low decrepitating quicklime (CaO) was attained at an optimum calcining temperature of 1000 °C at 5hrs as previously investigated in (Moropoulou, Bakolas, and Aggelakopoulou 2001). The first step is to mine high-purity limestone rock from Mugar, and the sample rocks will be crushed by using a ball milling machine to achieve the required particle size for processing. After that, the limestone will be calcined (heated) at 1000^{o}C, separating into lime (CaO) and carbon dioxide gas (CO_2).

$$CaCO_3 \xrightarrow{Heat} CaO + CO_2$$

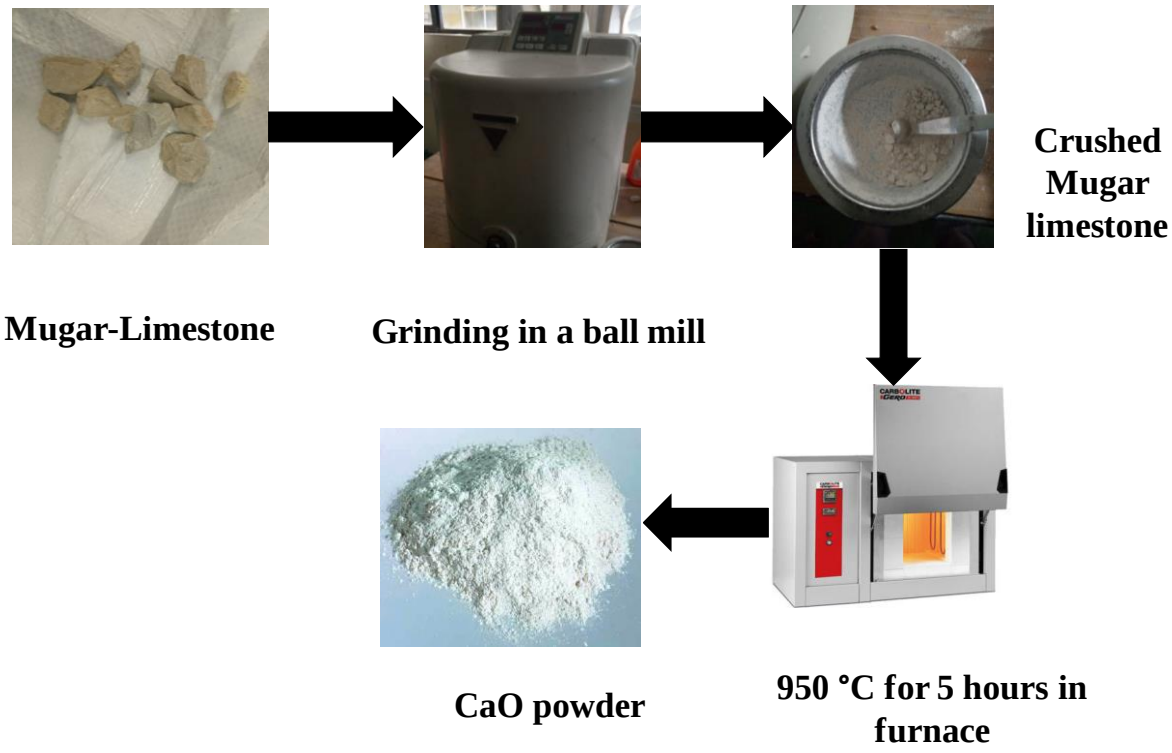

Figure 7.Illustration of quicklime synthesis

3.3 Preparation of slurry $Ca(OH)_2$

To prepare calcium hydroxide slurry powder, 10 grams of quick lime from Mugar was used instead of crushed limestone. The quick lime was calcined at 1000^{o}C to convert it into calcium oxide. 250ml of distilled water was then added to the calcium oxide to form a slurry using a stirrer and hot plate(Xie et al. 2023). The slurry was stirred continuously for a 30 minute dissolution time to ensure that the calcium oxide was completely hydrated and converted to calcium hydroxide(Mostafa et al. 2023). The resulting slaked lime was then filtered to remove any impurities. The filtered slurry was then dried using a drying oven at a temperature of 100 degrees Celsius for 24 hours to obtain calcium hydroxide slurry powder. The drying time and temperature were carefully controlled to ensure that the desired moisture content and particle size were obtained. The dissolution time and pH of the slurry were checked to ensure that the desired properties were obtained.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

3.4 Nano-PCC Formation by solution method

To synthesize Nano-Precipitated Calcium Carbonate (Nano-PCC) by solution method, the slaked lime obtained from the previous processes was used. Sodium carbonate was added to the slaked lime slurry in a round bottom flask equipped with a stirrer and a hot plate while stirring continuously(K. Seo et al. 2005) . The reaction between slaked lime and sodium carbonate resulted in the formation of Nano calcium carbonate precipitate, which was separated from the solution by filtration. The pH of the slurry was monitored and adjusted to maintain the desired pH level during the reaction. The use of a controlled pH was essential to ensure the formation of small and uniform-sized particles of Nano-PCC. After the completion of the reaction, the precipitate was washed and filtered using a vacuum filter to remove any impurities. The washing of the precipitate was done using distilled water to ensure the purity of the Nano-PCC). The filtered precipitate was then dried using a drying oven at a specific temperature and time to obtain Nano-PCC powder. The use of vacuum filtration for washing and filtering ensured the removal of any impurities and provided a high-quality Nano-PCC product. The specific equipment and steps used in this process may have varied depending on the scale of production and the desired properties of the Nano-PCC powder. Nano-PCC is a highly sought-after material due to its unique properties such as high surface area, small particle size, and uniform particle distribution. It finds applications in various industries such as paper, coatings, plastics, and biomedical. The controlled pH during the reaction and the use of vacuum filtration for

washing and filtering ensured the formation of small and uniform-sized particles of Nano-PCC, making it suitable for filler applications.

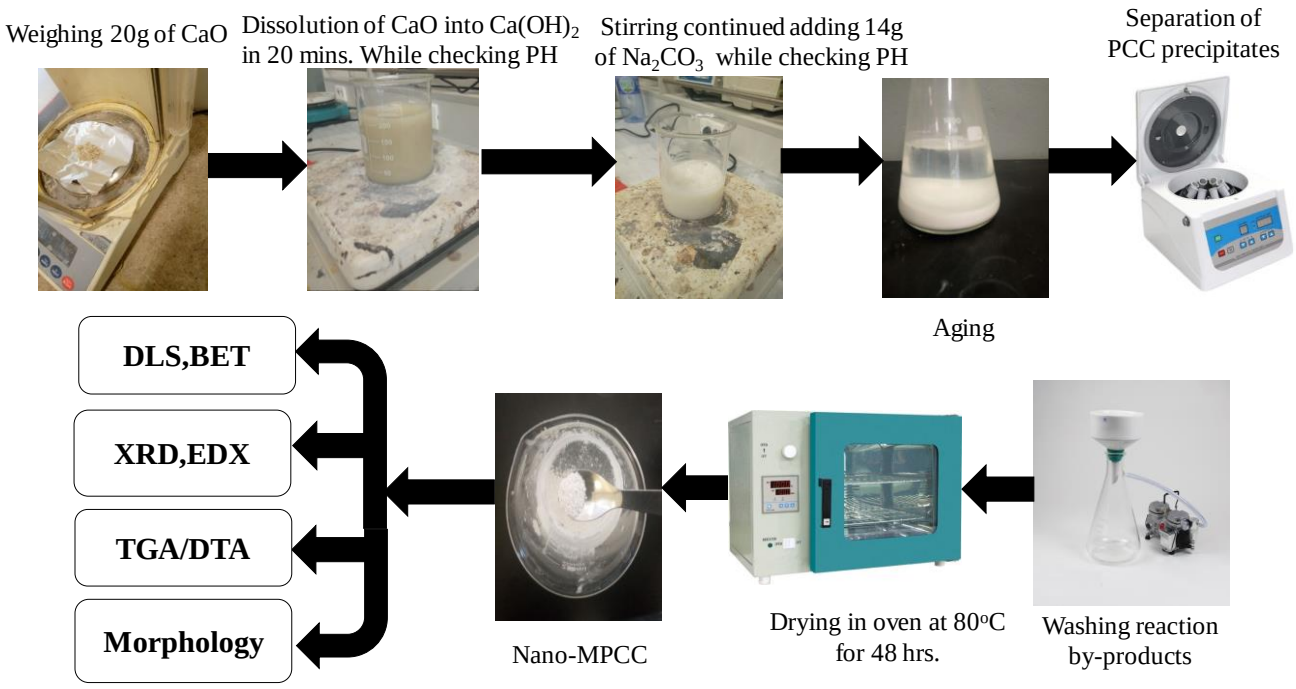

Figure 8.Experimental setup for the synthesis of MPCC Nano powders using Solution process

3.5 Extraction of Beef tallow fatty acids coater

The fat was extracted from the tissue by wet rendering as recommended by (Chilliard 1993).A mixture of animal matter: inedible offal, tissues, meat trimmings, waste and condemned meat, bones etc. were collected, shredded and reduced in sizes. The tallow fat is extracted using AOAC The AOAC 960.39 .The AOAC method 960.39 is a procedure used for the extraction of fats from solid samples using hexane as a solvent. In this method, a weighed sample of 5g is placed into a cellulose thimble and dried to eliminate any excess moisture that could interfere with the extraction process.

Hexane is then used as the extracting solvent, which is circulated around the sample in the thimble using a Soxhlet apparatus. The extraction process is typically continued for approximately 4 hours at a temperature of 70°C to ensure that all of the fat has been extracted from the sample.

Once the extraction is complete, the Soxhlet apparatus is removed and the solvent is evaporated from the extract. The remaining solid material is dried to remove any residual solvent(Cynthia T. Srigley and Magdi M. Mossoba 2017).

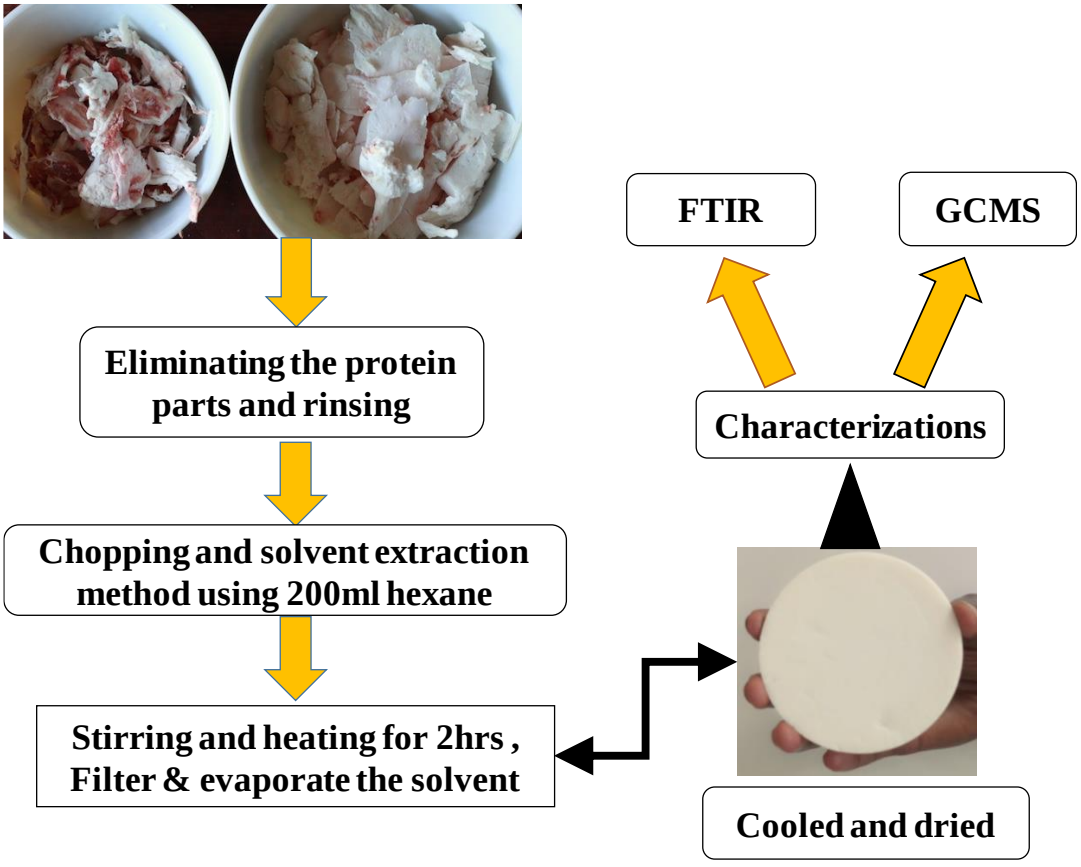

Figure 9. Illustration of tallow fatty acid rendering process

The fatty acid composition of a rendered tallow can have implications for its use in various applications, including as a coating material for nanoparticles in HDPE/PCC composites. The use of tallow in surface treatment can provide a sustainable and locally-sourced alternative to synthetic coating materials. By understanding the composition of fatty acids in tallow, it is possible to optimize the surface treatment of PCC nanoparticles and improve the compatibility and mechanical properties of HDPE/PCC composites.

Table 2.common fatty acid combinations in a rendered tallow(Nogoy et al. 2022)

Acid Name	%Composition
Miristic C14:0	2.79
Palmitic C16:0	26.78
Palmitoleic C16:1	2.05
Stearic C18:0	34.85
Oleic C18:1	30.23
Lenoleic C18:2	0.74

3.6 Coating or Surface Modification Method

100ml Heptane and rendered fatty acid tallow of 3g were mixed under stirring, then 5g of MPCC nanoparticle was added. The mixture was heated to 70°C under vigorous stirring for 4 hours. The solution was then filtered and the precipitate was rinsed thoroughly with a mixture of alcohol and deionized water. The precipitate was kept in a vacuum oven for 24h at 100°C. A white powder of tallow fatty acid-modified MPCC nanoparticles was obtained(SHENTU, LI, and WENG 2006).

3.7 Mixing and Composite Development

A smaller Polymix grinder(PX-MFC 90 D) was utilised to ensure uniform mixing and a high-quality composite material by blending virgin (HDPE) and precipitated calcium carbonate (PCC). The rotor speed kept constant for all combinations of PCC and also for the coated one the tallow percentage is constant 2g per 10g as well as mixing time . Below is the design of composites prepared.

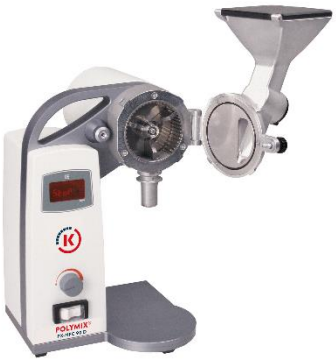

Figure 10. HDPE granules and PCC mixer (POLYMIX® PX-MFC 90 D)

Table 3. parameters and sample design

SR No	**Sample designation**	**HDPE (Wt%)**	**MPCC**	**Tallow**	**Mixing speed(rpm)**	**Temperature (^{O}C)**	**Time (mins)**
1	MPCC 0	100	0	0	3000	25	20
2	MPCC 10	90	10	0	3000	25	20
3	MPCC 20	80	20	0	3000	25	20
4	MPCC 30	70	30	0	3000	25	20
5	MPCC 40	60	40	0	3000	25	20
6	MCPCC20	80	20	10	3000	25	20

The parameter design table (Table 4) presents the sample designation and the corresponding parameter settings for the preparation of HDPE (high-density polyethylene) composite samples with varying weight percentages of MPCC (tallow fatty acid-coated precipitated calcium carbonate) and tallow (Barkoula et al., 2008; Cao et al., 2016; Pechyen and Ummartyotin, 2017). The selected parameter settings were based on previous studies and optimization efforts in the field of polymer composites.

Injection molding

The combination of HDPE and PCC was used in injection molding to produce HDPE/PCC composite tensile dog bone samples of ASTM D638 Type IV using the RR/TS injection molding machine. The HDPE and PCC were mixed in the desired proportions and loaded into the machine. The barrel temperature and tool temperature were set at 250°C and 60°C, respectively, and the injection pressure was set to 30Mpa with back pressure of 50bars. The holding time was 8 seconds. The molten HDPE/PCC mixture was injected into a mold cavity with the specific geometry of a dog bone and allowed to cool and solidify. Once the samples had solidified, their mechanical properties were evaluated.

Figure 11.Figure 10. RR/TS injection molding machine.

3.8 Characterizations

3.8.1 X-Ray Diffraction (XRD)

X-ray diffraction patterns of each sample were recorded by using a diffraction instrument (XRD- 7000S Shimadzu) with Cu Kα radiation, (Cu-Kα radiation λ = 1.5406 Å) using the operating voltage of 40 kV, a current of 30 mA, over the diffraction angle (2θ) range between 10° and 80°. Rietveld analysis (TOPAS 5, Bruker) of the XRD patterns was used to determine the structure and phase composition of the as-synthesized and thermally treated powders.

3.8.2 Fourier Transform Infrared Spectroscopy (FTIR)

The Nicolet™ iS50 FTIR instrument was employed in this study to analyze the functional groups present in Mugar precipitated calcium carbonate (MPCC) and tallow-coated MPCC (MCPCC) nanoparticles. The instrument was operated in the transmission mode, and the samples were prepared as KBr pellets. The spectra were collected in the range of 400-4000 cm^-1 with a resolution of 4 cm^-1. The FTIR spectra were used to identify the functional

groups in the samples and to investigate the effects of tallow coating on the surface chemistry of the particles.

3.8.3 Scanning Electron Microscopy (SEM)

In the study, SEM analysis was performed on the HDPE/PCC composite material to determine the morphology and microstructure of the composite. SEM analysis was necessary in the study because it provided valuable information about the microstructure and morphology of the HDPE/PCC composite material and basically the Nano powder morphology. This information helped to optimize the composite's processing conditions, such as temperature, pressure, and mixing time, for improved properties. Furthermore, SEM analysis provided insights into the interaction between the HDPE and PCC, and the effect of processing conditions on the microstructure of the composite. These insights were important for understanding the mechanism of composite formation and for developing strategies to improve the composite's properties.

3.8.4 Thermal Analysis

The Shimadzu DTG-60H (TGA + DTA) instruments was used in this study to investigate the thermal properties of Mugar precipitated calcium carbonate (MPCC) and tallow-coated MPCC (MCPCC) nanoparticles. The DTG measurements provided information about the weight loss and thermal decomposition behavior of the samples.

3.8.5 Differential Scanning calorimetry(DSC)

DSC measurements were taken with a Shimadzu DSC-60 Plus equipment in a nitrogen environment at a flow rate of 50 mL/min. The samples were heated at a rate of 10°C/min from 30°C to 600°C, and the heat flow was measured. The DSC curves were used to calculate the onset temperature, peak temperature, and enthalpy change.

3.8.6 GC-MS(Gas Chromatography-Mass Spectrometry)

For the evaluation of fatty acid profiles in animal tallow, (GC-MS) is a regularly used analytical technique. In these research, The GC-MS analysis was carried out using an Agilent GC system and a non-polar DB-5MS column (30 m x 0.25 mm x 0.25 m). The temperature programme began at 50°C for 1 minute, then ramped to 300°C at a rate of 10°C/min for 10 minutes. The

temperatures of the injector and detector were both set to 250°C. Helium was used as the carrier gas, with a flow rate of 1 mL/min.

3.8.7 Dynamic Light Scattering(DLS) and Image J

DLS is a widely used technique for determining the particle size distribution of suspended particles, including precipitated calcium carbonate (PCC) particles. The Malvern particle size analyzer, using Dynamic Light Scattering (DLS), was employed to measure the particle size and size distribution of Mugar precipitated calcium carbonate (MPCC) and tallow-coated MPCC (MCPCC) nanoparticles. Distilled water was used as the solvent for MPCC, while hexane was used for MCPCC. The instrument was operated at 25°C, and the scattering angle was set at 173°. The measurement duration was 120 seconds, and the data were collected at a rate of 10 kHz. The size distribution was obtained by analyzing the intensity autocorrelation function, and the hydrodynamic diameter was calculated using the Stokes-Einstein.

3.8.8 Mechanical Strength Testing

To conduct the tensile test, the specimens were made according to ASTM D638,type 4 standard, with the dimensions of 115 × 25 × 19 mm. The tensile test was conducted at room temperature with test speed of 5 mm/min using an WP10 Gunt universal test machine.

Figure 12. WP10 Gunt UTM

The WP10 Gunt tensile machine was used to evaluate the mechanical properties of the composite material. During this study, the HDPE/NanoPCC composite samples were prepared using injection molding techniques, and then subjected to tensile testing using the WP10 Gunt machine. The machine applied a controlled force to the samples, causing them to deform and ultimately fracture. The force and displacement data obtained from the test were used to calculate the tensile strength and modulus of elasticity of the composite material. The average values were calculated from five runs for each type of specimen.

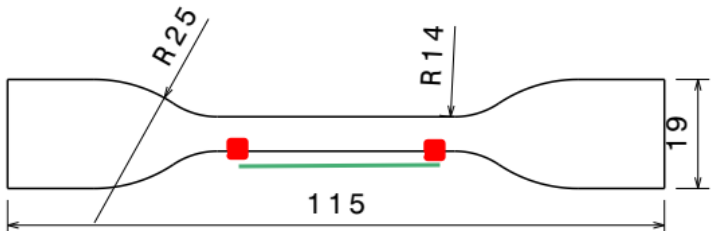

Figure 13.ASTMD638 Type IV sample parameter

CHAPTER FOUR

RESULT AND DESCUSSIONS

4.1 Thermal Analysis

The thermal analysis results show that the complete conversion of CaO to $Ca(OH)_2$ was achieved during the isothermal scan of $Ca(OH)_2$ up to 1000°C. The first onset occurred at 370°C, indicating the removal of physisorbed water, while the second onset occurred at around 410°C, indicating the removal of chemisorbed water. The onset observed at 640°C, corresponding to a mass loss of 29.6%, was due to the decomposition of calcium hydroxide to calcium oxide and water, as described by the following reaction.

$$Ca(OH) \rightarrow CaO + H_2O$$

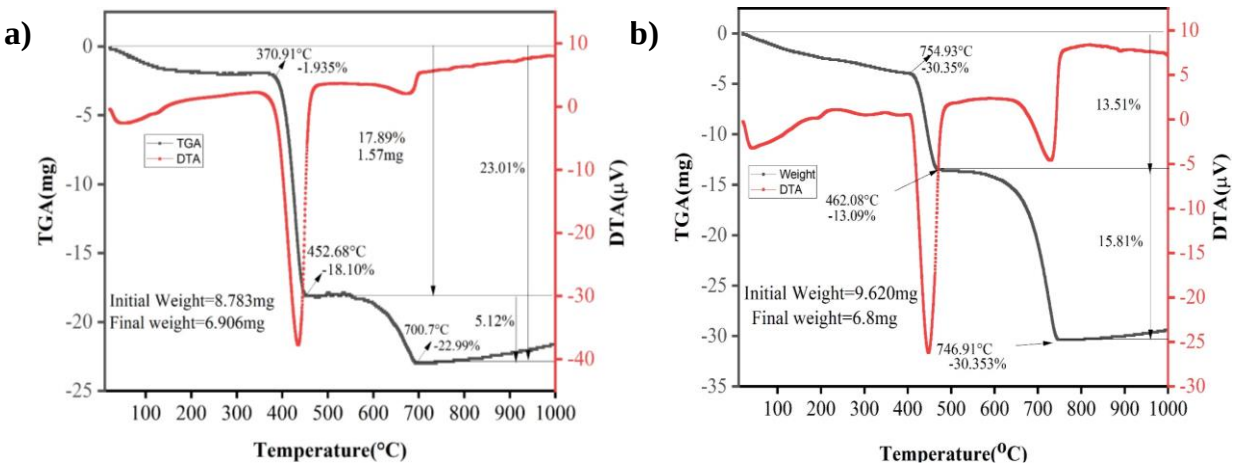

Figure 14.DTA, TGA of a) CaO (quik lime) from mugar limestone c) $Ca(OH)_2$ (slaked lime)

From Figure above a), DTA ,TGA curves have shown that Weight loss between 600 and 760°C is attributed to the decomposition of calcium carbonate contents which are CO_2 and CaO which is Quicklime. It confirms the high loss of mass between the above shown temperatures and the coincident endothermic peak in DTA curve. It confirmed that the Mugar lime stone is exhibiting the thermal behavior of calcite. The TGA analysis of MCPCC Nano powder showed a weight loss of -5.24% at temperatures between 400 and 800°C. The weight loss is likely due to the decomposition of the coating material and the organic compounds present on the surface of the Nano particles. The tallow fatty acid coating is expected to decompose at temperatures between

300 and 400°C, which could contribute to the weight loss observed in the TGA analysis. Additionally, the organic compounds present on the surface of the Nano particles could also decompose at higher temperatures, leading to further weight loss.

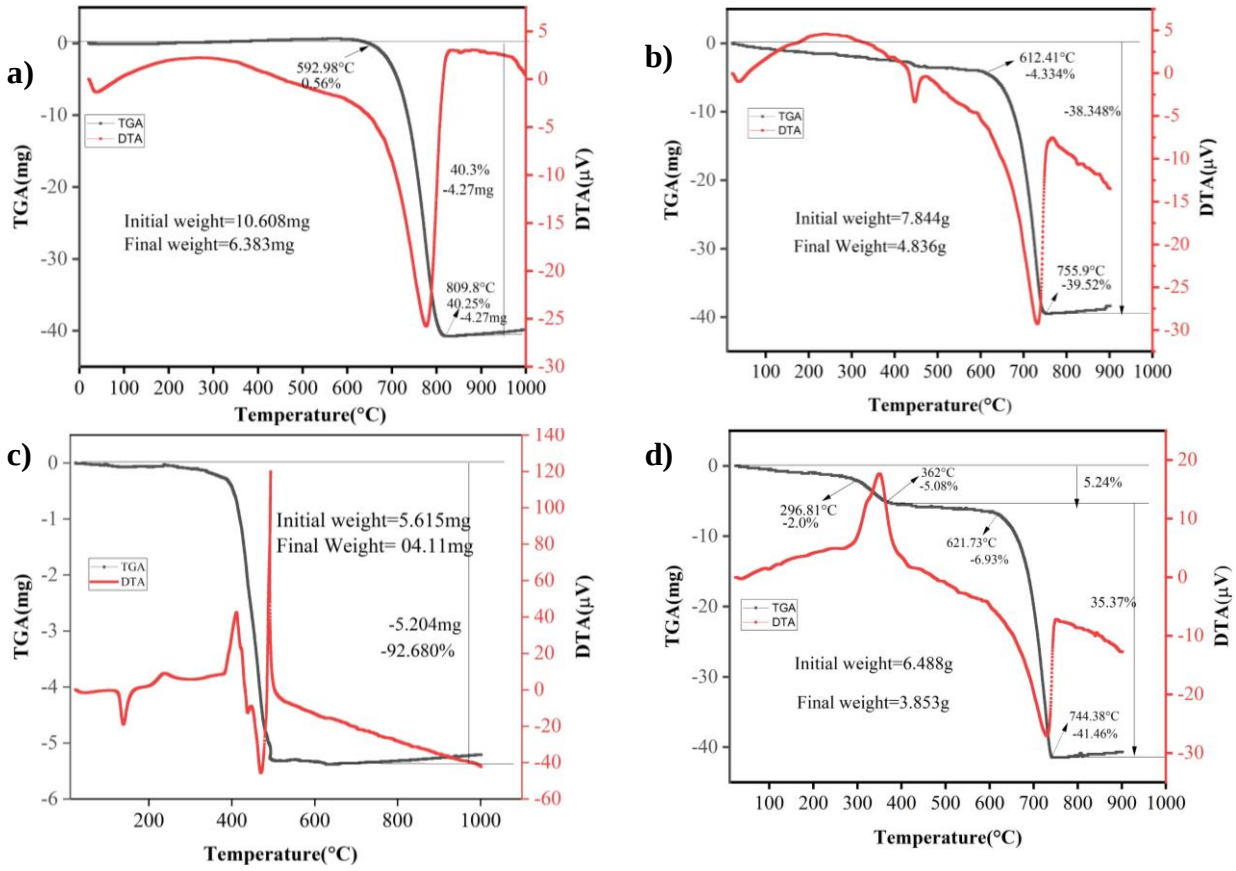

Figure 15. DTA, TGA of a)Mugar Limestone b)MPCC c) MPCC20 d) MCPCC powder

The TGA analysis of uncoated one, MPCC Nano powder showed a weight loss of 38.348% at temperatures between 400 and 800°C, which is lower than the weight loss observed for the tallow-coated PCC Nano powder. As mentioned earlier, the weight loss is primarily due to the decomposition of calcium carbonate present in the PCC Nano powder. The lower weight loss observed for the uncoated PCC Nano powder compared to the tallow-coated PCC Nano powder could be due to the presence of the coating material on the surface of the particles. The coating material can act as a barrier, preventing the release of gases during the decomposition of calcium carbonate and leading to a lower weight loss. Additionally, the coating can improve the thermal stability of the PCC Nano powder, reducing the amount of decomposition that occurs during the TGA analysis. The TGA and DTA analysis of HDPE/PCC Nano powder at

20wt% showed a total weight loss of -92.68%, which is a significant weight loss. This weight loss is primarily due to the thermal degradation of the HDPE polymer present in the Nano powder. The HDPE polymer undergoes a multi-step degradation process, with the main degradation occurring between 400 and 500°C. This results in the release of volatile gases such as hydrogen and methane, which contribute to the weight loss observed in the TGA analysis. The DTA curve shows a broad endothermic peak at around 400°C, which corresponds to the melting of the HDPE polymer. This is followed by a sharp exothermic peak at around 450°C, which corresponds to the onset of the main degradation process. Another possible interpretation of the weight loss observed in the TGA analysis could be due to the decomposition of the calcium carbonate ($CaCO_3$) present in the PCC Nano powder. However, the weight loss due to the decomposition of $CaCO_3$ would be expected to occur at temperatures above 600°C, which is higher than the temperatures observed in this analysis. Therefore, it is likely that the weight loss observed is primarily due to the thermal degradation of the HDPE polymer. The high weight loss observed in the TGA analysis could also be due to the presence of the PCC Nano powder. The PCC Nano powder can act as a nucleating agent, promoting the thermal degradation of the HDPE polymer. Additionally, the high surface area of the PCC Nano powder can increase the rate of reaction between the polymer and oxygen, leading to a more rapid degradation. Therefore, the presence of the PCC Nano powder in the HDPE matrix can contribute to the high weight loss observed in the TGA analysis

4.2Differential Scanning Calorimetry Results

The DSC results show that the MPCC20 sample had a melting temperature (T_m) of 135.82°C, a heat of fusion (ΔH_f) of 111.83 J/g, and a degree of crystallinity (X_c) of 62.33%. The 20wt% MCPCC sample had a slightly lower Tm of 134.61°C, but a higher ΔH_f of 126.62 J/g and a higher X_c of 70%. Finally, the 40wt% uncoated NanoPCC sample had a Tm of 134.61°C, a lower ΔH_f of 70.2 J/g, and a lower X_c of 38%. The percent crystallinity of HDPE in the composites were calculated as follows:

$$X_C(\text{HDPE})=\frac{\Delta H}{W(HDPE)\times\Delta H^{\circ}}$$

Where ΔH (composite) is the apparent enthalpy of fusion per gram of composite, ΔH°(HDPE) is the heat of fusion of 100% crystallinity HDPE, taken as 200 J/g from(Wunderlich 1997) , and W(HDPE) is the weight fraction of HDPE in the composite

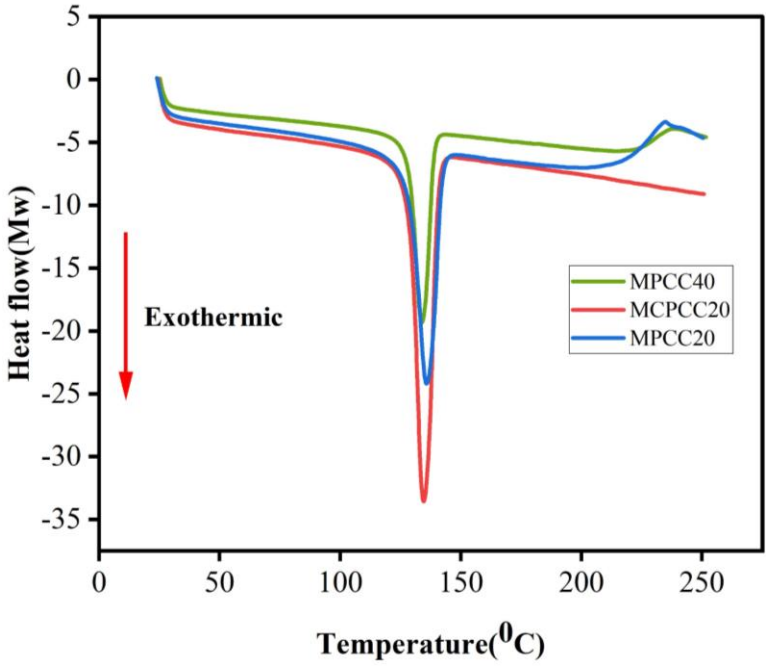

Figure 16. DSC results summary of three sample comparison

Based on these specific numbers, we can see how the concentration of MPCC fillers affect the thermal behavior and degree of crystallinity of the HDPE nanocomposites. The higher ΔH_f and Xc values of the MCPCC sample compared to the MPCC samples suggest that the coating improved the interfacial adhesion between the fillers and polymer matrix, resulting in better dispersion of the fillers and a more ordered crystal lattice. The lower Xc value of the 40wt% MPCC sample compared to the 20wt% samples indicates that at higher filler concentrations, there may be a saturation point beyond which the degree of crystallinity does not continue to increase.

Table 4. DSC results summary of three sample comparison

Samples	T_m(^{O}C)	ΔH_f J/g	X_c(%)
MPCC20	135.82	111.83	62.33
MCPCC20	134.61	126.62	70
MPCC40	134.61	70.2	38

4.3 Particle Size Analysis

The DLS examination of MCPCC particles reveals only clusters with a narrow size distribution, it indicates that the tallow coating is efficient in lowering interparticle attraction forces and preventing the formation of large, tightly bonded agglomerates. The DLS measurements of tallow-coated and uncoated neat PCC showed significant differences in their particle size distribution. The uncoated PCC particles exhibited a bimodal distribution with two distinct peaks at 40-60 nm and 140 nm, while the tallow-coated PCC particles showed a broader distribution with a single peak at 100-120 nm. The polydispersity index (PDI) values for the uncoated and tallow-coated PCC samples were 0.34 and 0.5, respectively as indicated in previous researches(Tsuzuki, Pethick, and McCormick 2000). The results of our DLS analysis suggest that the coating of PCC particles with tallow leads to an increase in their mean particle size and a broader particle size distribution. This may be attributed to the adsorption of tallow molecules onto the surface of PCC particles, which can lead to the formation of agglomerates or clusters(Racca et al. 2019).

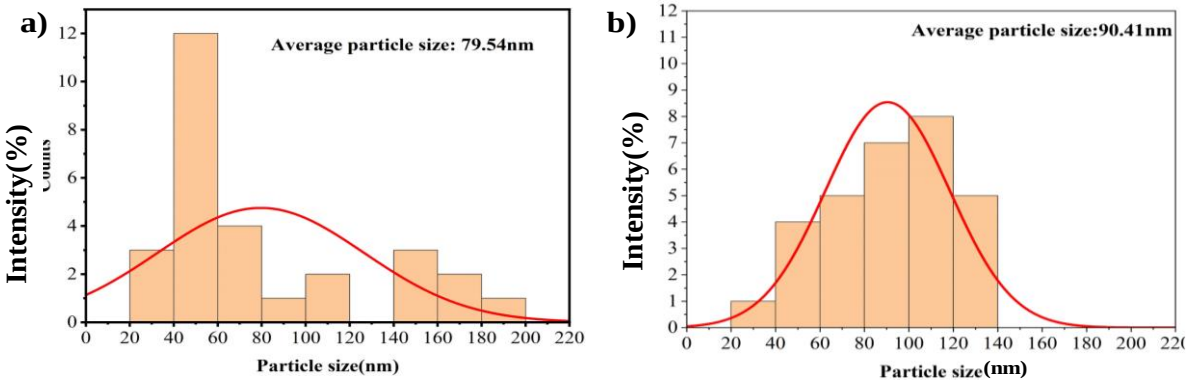

Figure 17. a)Average particle size of MPCC b)Average particle size of MCPCC

The broader size distribution observed for MCPCC may indicate the presence of larger agglomerates or clusters in the sample. The bimodal size distribution observed for MPCC may be due to the presence of different types or sizes of particles in the sample, such as aggregates or impurities. The presence of smaller particles in MPCC may also be indicative of the presence of PCC nanoparticles or nanoclusters, which are known to exhibit unique properties compared to larger PCC particles.

The unimodal distribution of MCPCC particles, with a very small and a slightly larger size distribution, may be a result of the coating process and the interactions between the tallow molecules and the PCC nanoparticles as reported in (Sulimai et al. 2016). The bimodal distribution in DLS of uncoated PCC can be attributed to the presence of two distinct populations of particles with different sizes in the solution. This can occur due to several reasons. One possible explanation for the bimodal distribution is that the PCC particles have agglomerated or aggregated during sample preparation, resulting in larger particles that are not fully dispersed in the solution. These larger particles may contribute to a second peak in the particle size distribution, resulting in a bimodal distribution. It is also possible that the bimodal distribution is the result of different crystal forms of calcium carbonate in the PCC sample. Different crystal forms of calcium carbonate, such as calcite and aragonite, have different sizes and shapes, which can result in distinct populations of particles in the solution(Siva et al. 2017).

4.4 Phase analysis

To distinguish between minerals from the calcite group and another polymorphs Namely, Aragonite and vaterite, the rather intense diffraction maximum in calcite appear at around $2\theta = 30°$. The analysis of the X-ray diffraction shows that the structure is hexagonal with space group. Unit cell parameters are: a = 4.988 Å, c = 17.06 Å and $\gamma = 120°$. The X-ray diffraction spectrum comparison is seen below. The values of the inter-reticular distance of the sample spectrum are reported and are compared also with those of the literature. These results indicate that the sample consists exclusively of calcite because no trace of another phase was highlighted. The XRD pattern as shown in Figure below completely supported about our conclusion that CaO transformed successfully from Mugar Limestone in this experimental work ; it coincided with JCPDS card : 00-037-1497, which appearing in the specific pattern of 2θ at 18.0166°, 38.1182° and 50.8479° reflected on the specific XRD pattern of CaO crystal.

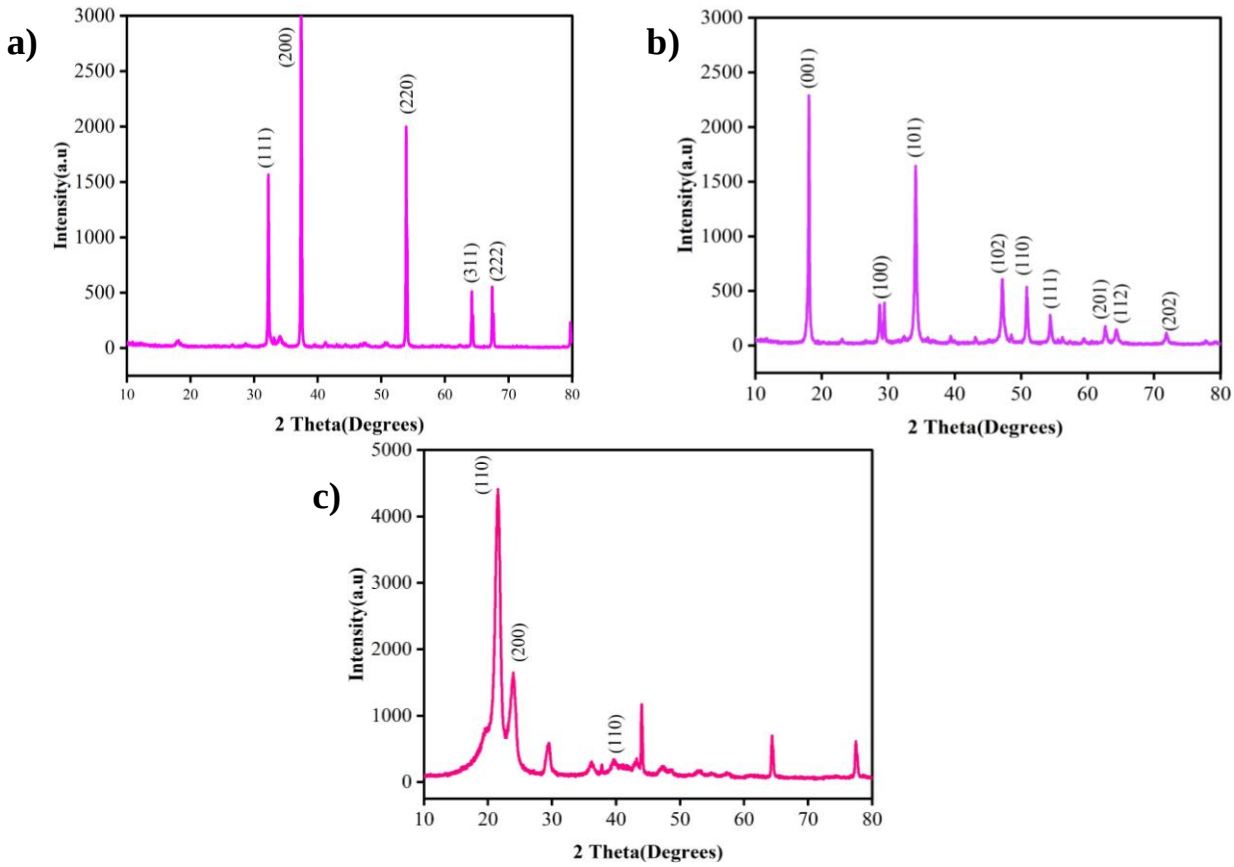

Figure 18. XRD of a) Quicklime from Mugar limestone(CaO) after calcined at 1000^0C b)slaked lime($ca(OH)_2$ c)HDPE/MPCC20 composite

Based on the three highest intensities, it had been detected at 2θ of 34.1182°, 18.0166° and 50.8479°. While all the peaks coincide the JCPDS Card No: 00-004-0733, a minor peak (red dot) detected at 2θ=29.3 which corresponds to (104) plane of rhombohedral calcite phase with space group R-3c since the portlandite $Ca(OH)_2$ reacted with CO_2 gas from the surrounding air and calcite is formed as second phase . X-ray diffraction (XRD) analysis of HDPE shows a broad halo centered around 2θ values of 20-25°, which is characteristic of the amorphous

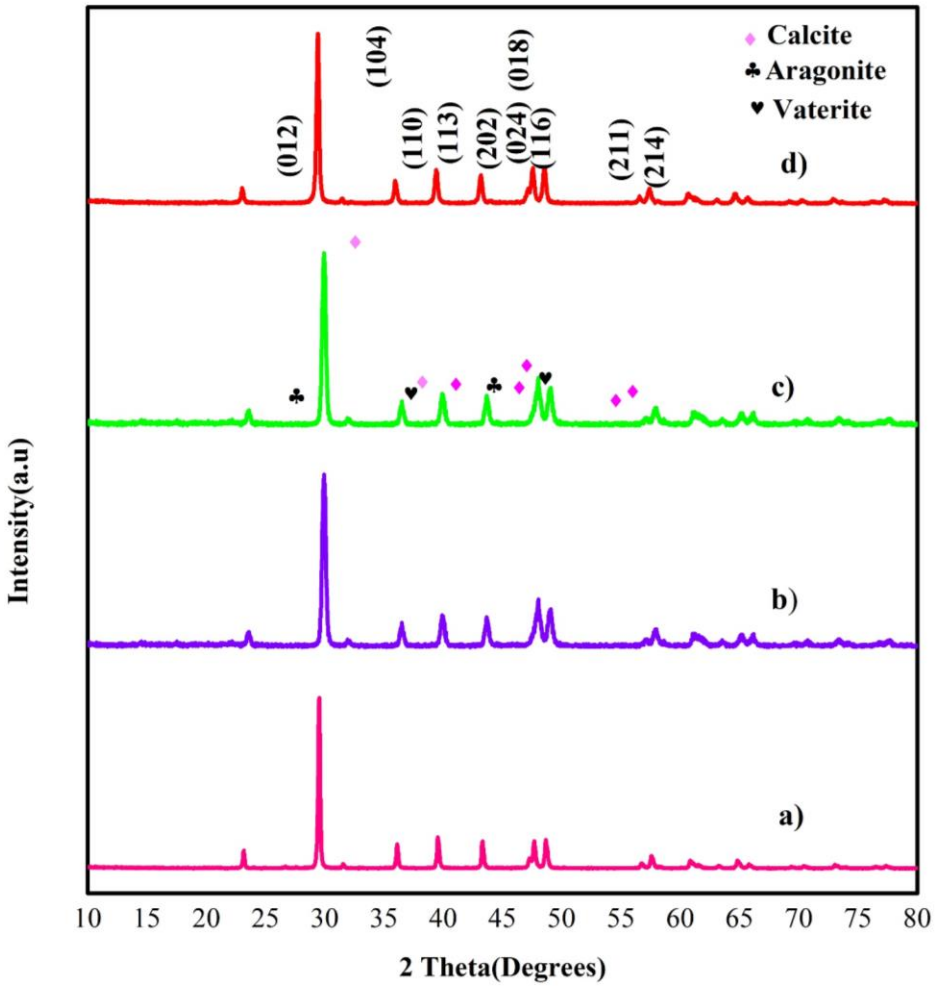

Figure 19. XRD of a)Mugar raw limestone b)Commercial Masteratch c)MPCC d)MCPCC

regions in the polymer. The XRD pattern may also show low-intensity peaks around 2θ values of 21.5°, 23.9°, and 28.5°, corresponding to the (110), (200), and (222) planes, respectively, which are characteristic of the crystalline regions in the polymer. These peaks can be used to confirm the crystalline structure of HDPE. However, the XRD pattern of HDPE is dominated by the amorphous halo due to the random molecular arrangement of the polymer.

Indicated in the Figure.15; the XRD phases of Mugar limestone are similar to the commercial masterbatch. This suggests that Mugar limestone may be a suitable replacement for the commercial masterbatch in certain applications. Additionally, the tallow fatty acid coated Mugar PCC showed no difference with the uncoated Mugar PCC, indicating that the coating surfactant is inert and does not change the chemistry of the filler but only enhances the surface property. This result suggests that the coating surfactant could be used to improve the surface properties of Mugar PCC without altering its chemical composition. Overall, these findings provide valuable insights into the potential use of Mugar limestone and tallow fatty acid coated Mugar PCC in various applications.

4.5 Functional Group Analysis by FTIR

Because virgin HDPE (high-density polyethylene) is mostly composed of carbon and hydrogen atoms, it lacks any major functional groups detectable by FTIR. The distinctive peaks associated to the vibrational modes of the CH_2 groups in the polymer backbone dominate the FTIR spectra of virgin HDPE. These peaks provide information about the polymer's molecular structure and can be used to identify and characterize various polyethylene materials.

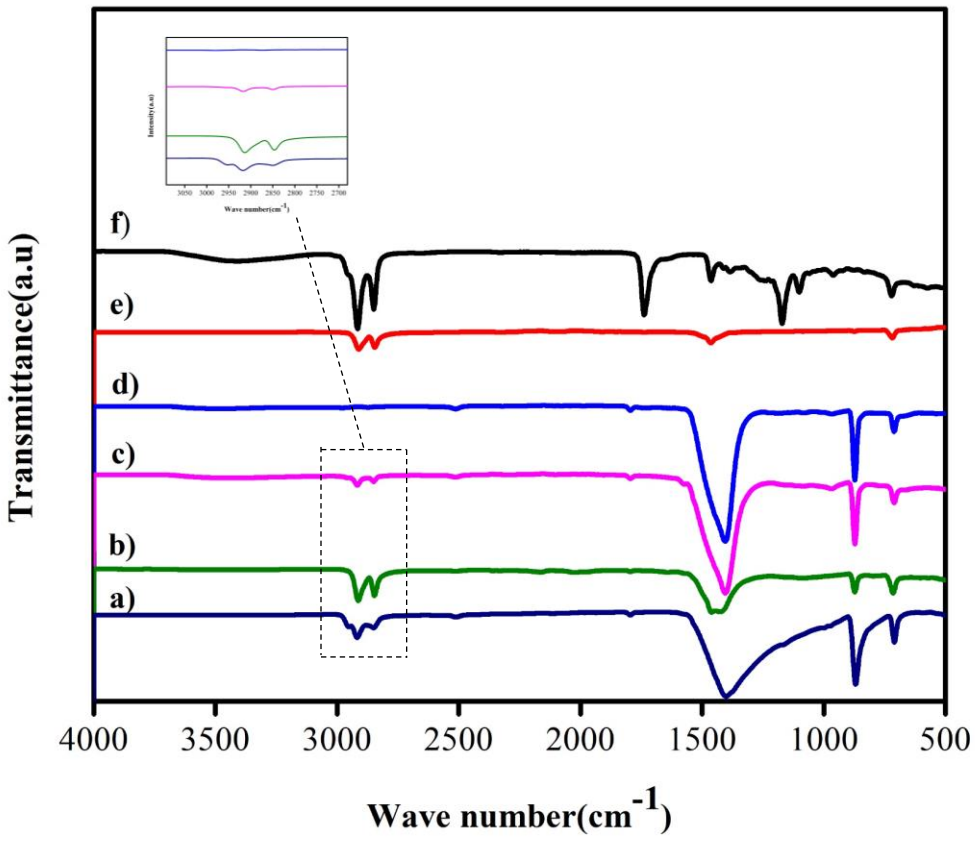

Figure 20.a)Commercial Masterbatch b)MCPCC20 c)MCPCC d)MPCC e)Pure HDPE(MPCC0) f)Tallow

For the pure HDPE a strong peak in the 2850-2960cm^{-1} range, which is associated with the stretching vibrations of C-H bonds in the methylene (-CH_2-) groups of the polyethylene chain. A peak in the 1460-1470cm^{-1} range, which is associated with the bending vibrations of C-H bonds in the methylene (-CH_2-) groups of the polyethylene chain. A peak in the 720-740cm^{-1} range, which is associated with the rocking vibrations of the methylene (-CH_2-) groups of the polyethylene chain. A peak in the 1370-1380 cm^{-1} range, which is associated with the bending vibrations of C-H bonds in the methyl (-CH_3) groups of the polyethylene chain(Elkhouly et al. 2022). A peak in the 730-800 cm^{-1} range, which is associated with the out-of-plane bending vibrations of the aromatic rings in the additives and impurities in the sample. Overall, the FTIR spectrum of virgin HDPE is relatively simple and contains only a few peaks. The absence of broad peaks in the 3000-3600 cm^{-1} range indicates that there are no significant amounts of hydroxyl or amine functional groups present in the sample. The spectrum is dominated by peaks associated with the polyethylene chain, which is the main component of the material. The FTIR

spectra of uncoated PCC and coated PCC by tallow show differences due to the presence of functional groups associated with the tallow coating. The FTIR spectrum of uncoated PCC shows characteristic peaks related to the vibrational modes of the carbonate ion (CO_3) in the PCC crystal lattice. The FTIR spectrum of MCPCC exhibits characteristic peaks in the 1420-1480 cm-1 and 870-890 cm-1 regions, which are attributed to the bending and stretching vibrations of the CO_3 ion, respectively. In addition, the presence of tallow coating results in the emergence of new peaks in the FTIR spectrum. These peaks correspond to the functional groups present in the tallow coating, such as the stretching vibrations of the CH_2 groups in the tallow coating (2800-3000 cm^{-1}), the stretching vibrations of the carbonyl (C=O) group in the tallow coating (1740-1760 cm^{-1}), the bending vibrations of the CH_2 groups in the tallow coating (1450-1470 cm^{-1}), and the rocking vibrations of the CH_2 groups in the tallow coating (720-740 cm^{-1}). The FTIR spectrum of the composite material will shows the characteristic peaks of HDPE, tallow, and PCC, as well as any new peaks that may arise due to chemical reactions or interactions between the components. Here are some possible interpretations of the FTIR spectrum(Thenepalli et al. 2015). The FTIR spectrum of pure HDPE typically shows peaks at around 2917 cm^{-1} and 2849 cm^{-1}, which correspond to the stretching vibrations of the CH_2 groups in the polymer backbone. The presence of peaks in the composite spectrum at around 1435cm^{-1} and 872cm^{-1}, corresponding to the bending vibrations of the carbonate ion, indicates the presence of PCC in the material, while the presence of additional peaks in the same spectrum indicates the presence of tallow in the composite.

4.6 GCMS Results of Tallow fatty acid analyzing

The GCMS analysis of the animal tallow sample revealed the presence of two fatty alcohols, including 1-Dotriacontanol and octadecane, which indicate the presence of their corresponding fatty acids, behenic acid and stearic acid, at retention time of 7.667 and 9.388respectively. 1-Dotriacontanol is a fatty alcohol that is derived from the reduction of behenic acid, a long-chain saturated fatty acid with a chain length of 22 carbons that is commonly found in animal fats, including tallow(Mudge 2005). The appearance of 1-Dotriacontanol in the GCMS data suggests the presence of behenic acid in the animal tallow sample. Similarly, octadecane is a fatty alcohol that is derived from the reduction of stearic acid, a long-chain fatty acid with a chain length of 18 carbons. The identification of 1-Dotriacontanol and octadecane in the animal tallow sample

provides additional information about the composition of the sample and the presence of their corresponding fatty acids, behenic acid, and stearic acid, respectively(Harvey 1989).

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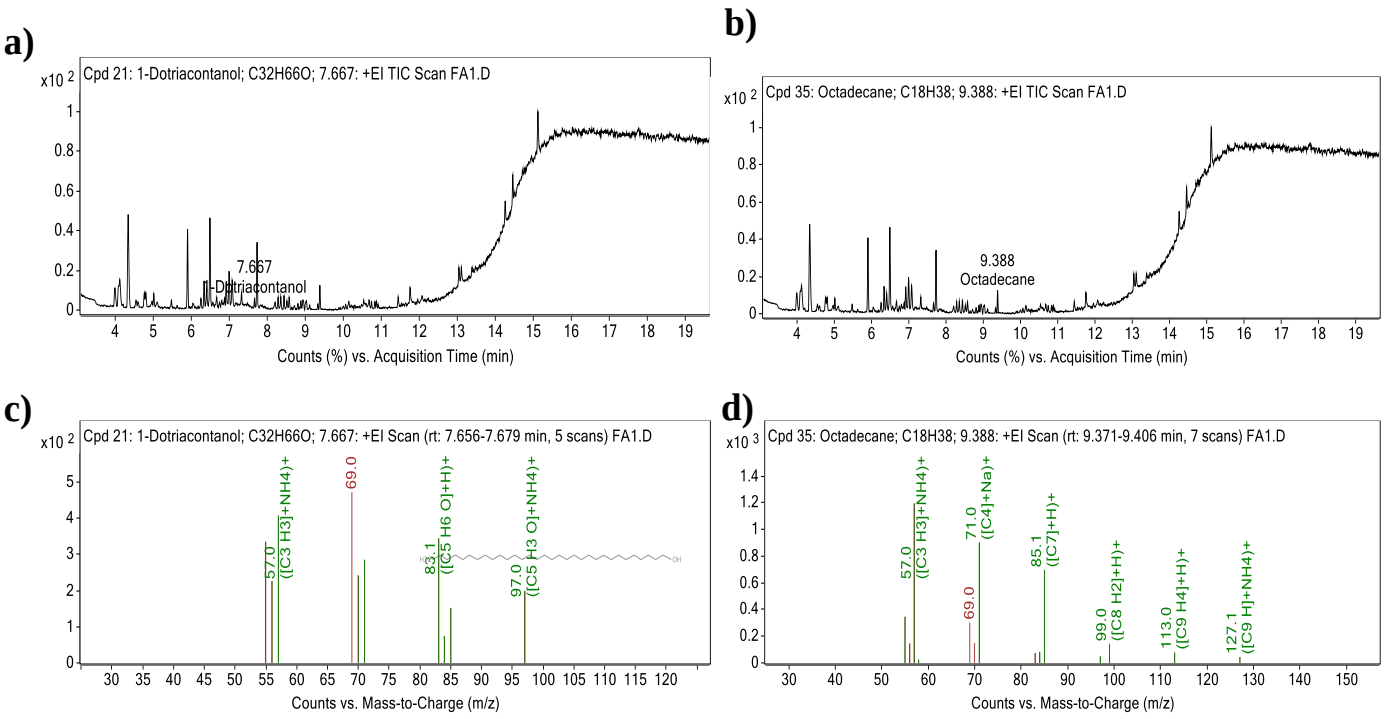

Figure 21. Figure 19. a)Counts Vs Acquisition time for 1-Dotriacontanol b) Octadecane c) Counts Versus Mass to charge ratio of 1-Dotriacontanol d)Octadecane

4.8 Tensile Results

The tensile strength of the HDPE/MPCC composites increased as the weight percentage of Nano PCC increased. The composite with 0wt% PCC has a tensile strength of 15.47 MPa. The addition of 10wt% Nano PCC increases the tensile strength to 16.41 MPa, an increase of approximately 6.1% compared to the 0wt% composite. Further increasing the weight percentage of PCC to 20wt% results in a tensile strength of 18.75 MPa, a 14.3% increase from the 10wt% composite. The composite with 30% PCC has a tensile strength of 18.23 MPa, a slight decrease of 2.2% from the 20wt% composite, while the composite with 40% PCC has a tensile strength of 18.22 MPa, a further decrease of 0.05%. The increase in tensile strength with increasing weight percentage of PCC can be attributed to the reinforcing effect of the Nano PCC particles(Lazzeri et al. 2005a). The PCC particles act as a reinforcement in the composite,

increasing the strength and stiffness of the material(Rothon 2017). As the weight percentage of PCC increases, there are more particles present in the composite, leading to a greater reinforcing effect and improved mechanical properties such as tensile strength until certain optimium concentration (Bartczak and Galeski 2014). The decrease in tensile strength observed in the composite with 30% PCC and 40% PCC may be due to the presence of an excessive amount of PCC particles, which can lead to agglomeration and poor dispersion in the matrix. This can result in defects and weak points in the composite, which can reduce its overall mechanical strength. The processing conditions used to produce the HDPE/PCC composites can also affect the mechanical properties. In this case, the composites were mixed on a POLYMIX® PX-MFC 90 D at a temperature of 25^{o}Cand an RPM of 3000. The mixing conditions can affect the dispersion of the PCC particles in the HDPE matrix, which in turn can affect the mechanical properties of the composite. Figure 21.shows the dog bone specimens done for optimization .It is important to optimize the processing conditions to achieve uniform dispersion and maximize the reinforcing effect of the PCC particles(Kherici, Benouali, and Nouredine 2022).

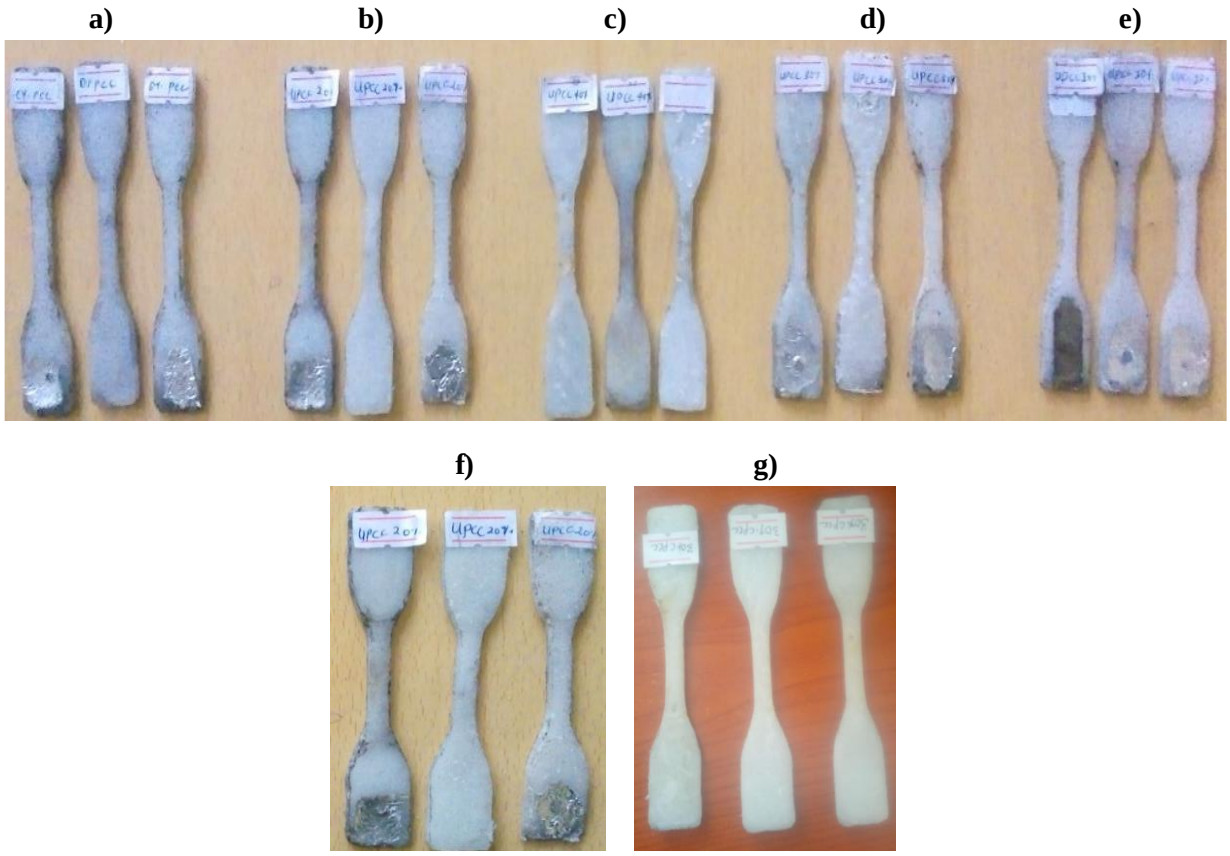

Figure 22.Tensile Dog bones of ASTMD638 type IV a)MPCC0 b)MPCC20 c)MPCC10 d)MPCC30 e)MPCC40 f) MPCC20 and g)MCPCC20

The composite MCPCC20 has the highest tensile strength, with a value of 19.79 MPa. This is a 5.5% increase compared to theMPCC20, which has a tensile strength of 18.75 MPa. The increase in tensile strength observed with the MCPCC20 Combination can be attributed to several factors. The coating of the Nano PCC particles with tallow fatty acids can improve the dispersion of the particles in the HDPE matrix, which can enhance the reinforcing effect of the particles. Additionally, the coating can improve the interfacial adhesion between the particles and the matrix, which can lead to more effective stress transfer and increased mechanical strength(Huang et al. 2013). The tallow fatty acids used to coat the Nano PCC particles can also act as a compatibilizer between the PCC particles and the HDPE matrix. This can improve the wetting and spreading of the particles in the matrix, which can further improve the reinforcing effect of the particles and increase the mechanical strength of the composite.

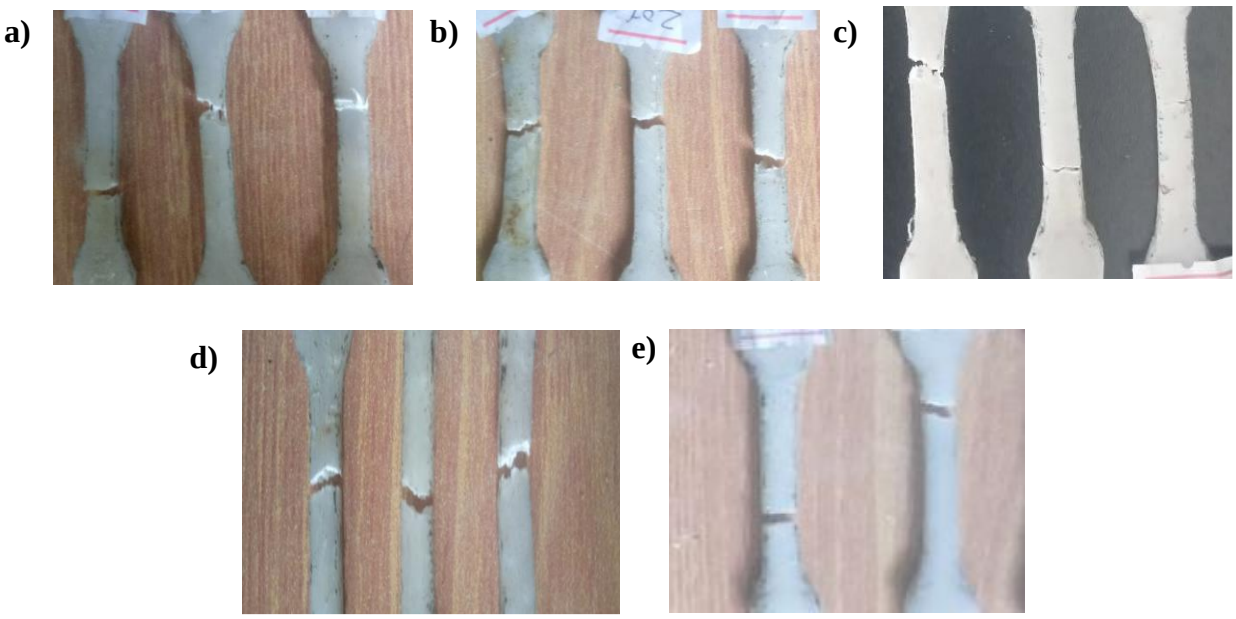

Figure 23.After Test a)MPCC10 b)MPCC20 c)MCPCC20 d) MPCC30 e)MPCC0

The toughness modulus of the HDPE/MPCC composites generally increased as the weight percentage of MPCC increased. The composite with neat HDPE has a toughness modulus of 23.37 KJ/m^3. The addition of 10wt% MPCC increases the toughness modulus to 28.06 KJ/m^3, an increase of approximately 19.9% compared to neat HDPE. Further increasing the weight percentage of uncoated one, MPCC to 20wt% results in a toughness modulus of 29.24 KJ/m^3, a 4.2% increase from the 10wt% composite. Coating the 20wt% MPCC particles with tallow fatty acids increases the toughness modulus to 33.43 KJ/m^3, a significant increase of 14.2% compared to the uncoated 20wt% MPCC composite. The composite with 30% MPCC has a toughness modulus of 25.24 KJ/m^3, a decrease of 14.0% from the 20wt% composite, while the composite with 40% uncoated Nano PCC has a toughness modulus of 26.77 KJ/m^3, a slight increase of 6.1% from the 30wt% composite. The increase in toughness modulus with increasing weight percentage of Nano PCC can be attributed to the reinforcing effect of the PCC particles(Khalaf 2015). However, the decrease in toughness modulus observed with the 30wt% uncoated Nano PCC composite and the slight increase in the 40wt% uncoated Nano PCC composite may be due to the presence of an excessive amount of PCC particles, which can lead to agglomeration and poor dispersion in the matrix(Qingxiu Li and Matuana 2003). This can result in defects and weak points in the composite, which can reduce its overall toughness modulus. The specific mechanical properties of the composite can be affected by

various factors such as the size, shape, and distribution of the PCC particles, as well as the processing conditions used to produce the composite. The Young's modulus of the HDPE/Nano PCC composites generally increases as the weight percentage of Nano PCC increases. The composite with neat HDPE has a Young's modulus of 88.09 ± 1.99 MPa. The addition of 10wt% uncoated Nano PCC increases the Young's modulus to 128.12 ± 7.50 MPa, an increase of approximately 45.5% compared to neat HDPE. Further increasing the weight percentage of uncoated Nano PCC to 20wt% results in a Young's modulus of 131.53 ± 5.34 MPa, a 2.7% increase from the 10wt% composite. Coating the 20wt% Nano PCC particles with tallow fatty acids increases the Young's modulus to 204.45 ± 44.99 MPa, a significant increase of 55.4% compared to the uncoated 20wt% Nano PCC composite. The composite with 30% uncoated Nano PCC has a Young's modulus of 131.32 ± 3.08 MPa, a slight decrease of 0.1% from the 20wt% composite. The composite with 40% uncoated Nano PCC has a Young's modulus of 254.17 ± 2.34 MPa, a further increase of 93.4% from the 30wt% composite. The increase in Young's modulus with increasing weight percentage of Nano PCC can be attributed to the reinforcing effect of the PCC particles(Teixeira et al. 2006).

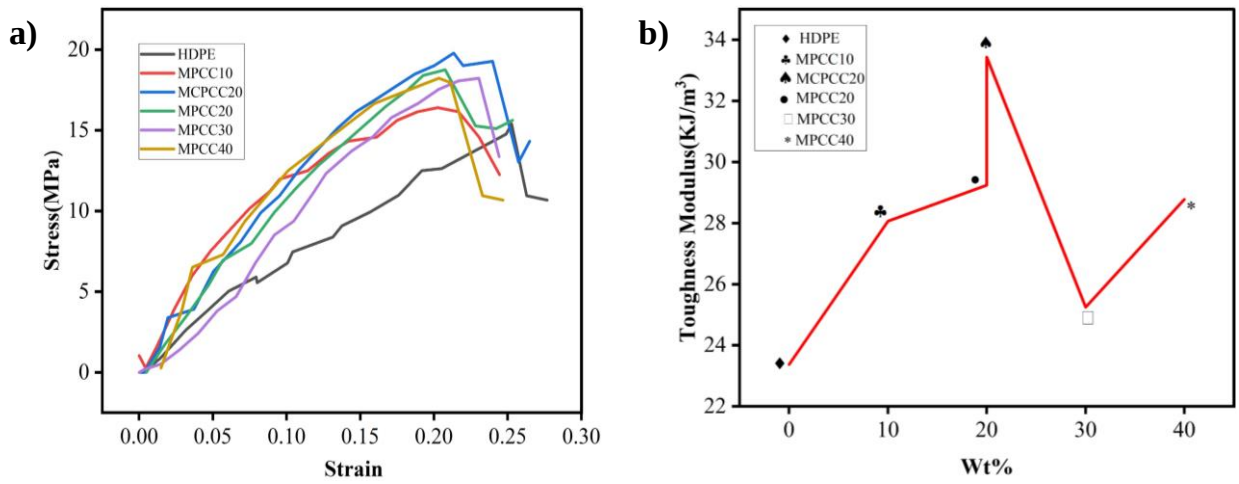

Figure 24.a) Stress Strain results b)Toughness Moduli Results

The PCC particles act as a reinforcement in the composite, increasing its stiffness and overall strength. As the weight percentage of PCC increases, there are more particles present in the composite, leading to a greater reinforcing effect and improved mechanical properties such as Young's modulus(Katančić et al. 2014). The significant increase in Young's modulus observed with the 20wt% Nano PCC coated with tallow fatty acids can be attributed to the coating's ability to improve the interfacial adhesion between the particles and the HDPE matrix. This can

lead to more effective stress transfer and increased mechanical strength. The slight decrease in Young's modulus observed with the 30wt% uncoated Nano PCC composite may be due to the presence of an excessive amount of PCC particles, which can lead to agglomeration and poor dispersion in the matrix. This can result in defects and weak points in the composite, which can reduce its overall Young's modulus.

Table 5. Results of Mechanical properties

SR No	**Sample designation**	**Tensile Strength(Mpa)**	**Toughness moduli(KJ/m^3)**	**Young's Moduli (Mpa)**
1	MPCC 0	15.46528	23.3698	88.08928 ± 1.99229
2	MPCC 10	16.40625	28.0606	128.11892 ± 7.49541
3	MPCC 20	18.75	29.2376	131.52998 ± 5.34487
4	MCPCC 20	19.79167	33.4314	204.45484 ± 44.98531
5	MPCC 30	18.23	25.2449	131.32399 ± 3.08182
6	MPCC40	18.22	26.7748	254.17131 ± 2.337490

4.9 Morphology

In the comparison between tallow-coated and uncoated PCC, it was found that the tallow-coated PCC exhibited a higher degree of clustering while maintaining very low agglomeration, in contrast to the uncoated PCC that displayed more agglomeration. The clustering of tallow-coated PCC can be attributed to the hydrophobic nature of the tallow coating, which promotes inter-particle interactions and enhances the propensity of the particles to cluster together. This phenomenon is likely due to the fact that the tallow coating reduces the surface energy of the PCC particles, resulting in a reduction in their affinity for water and an increase in their tendency to cluster. On the other hand, the greater agglomeration observed in uncoated PCC may be attributed to various factors such as the presence of moisture during processing, the high surface energy of the PCC particles, or the presence of impurities. These factors may promote sticking and coalescence of the PCC particles, leading to agglomeration. It is important to note that while tallow-coated PCC particles may exhibit a higher degree of clustering, this

does not necessarily translate to poor dispersion in applications. In fact, the low agglomeration observed in tallow-coated PCC particles may have positive implications for their dispersion in various applications, such as coatings and plastics, as they are less likely to form large, unwanted aggregates that can negatively affect product performance. In summary, tallow-coated PCC particles exhibit a higher degree of clustering but low agglomeration, whereas uncoated PCC particles demonstrate more agglomeration. The clustering of tallow-coated PCC is attributed to the hydrophobic nature of the tallow coating, while the agglomeration of uncoated PCC may be due to various factors such as moisture, surface energy, or impurities.

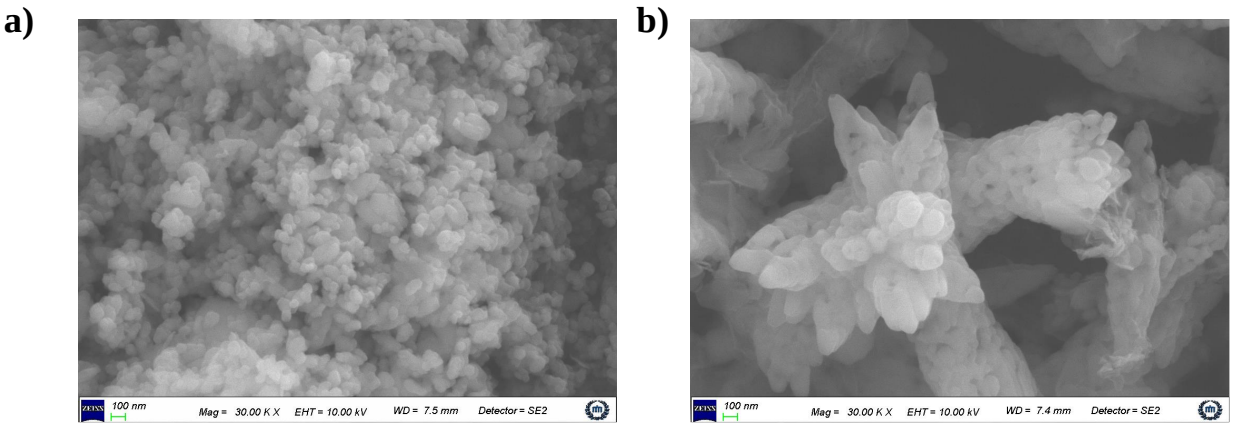

Figure 25. SEM Morphology of a) MPCC powder b) MCPCC powder

A PCC can have both low agglomeration and strong clustering. In fact, clustering and agglomeration are two separate processes that can occur in particle systems at the same time. The tendency of particles to aggregate or form clusters as a result of attractive inter-particle forces is referred to as clustering. Clustering occurs when particles are drawn together due to surface chemistry, shape, or size. Clustering can result in the development of small, well-defined clusters of particles bound together only loosely. Agglomeration, on the other hand, is the process by which particles adhere to one another to create larger structures or aggregates. A range of variables, including van der Waals forces, electrostatic attraction, and capillary forces, can cause agglomeration.

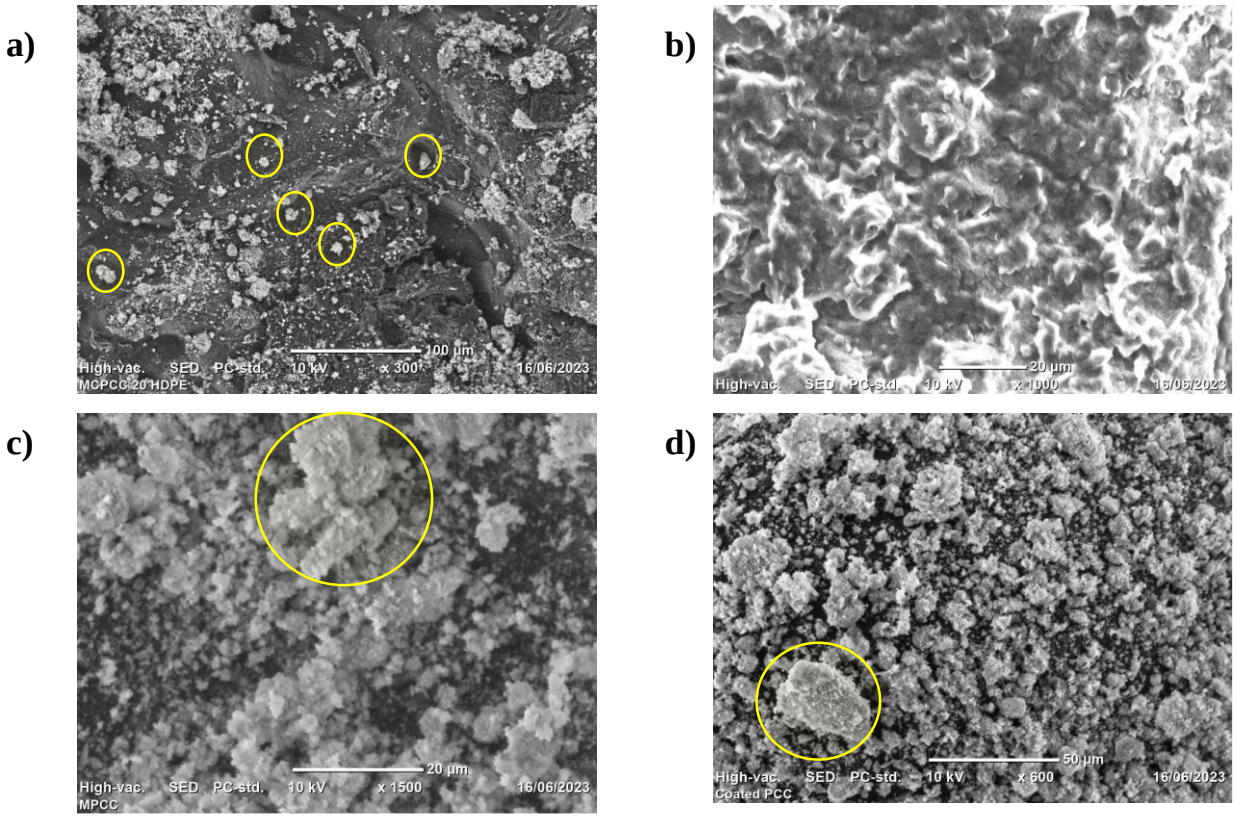

Figure 26. SEM images a)fractured tensile sample of MCPCC20 b)Neat HDPE c) MPCC Nanopowder d) MCPCC nanopowders

The SEM images in the Figure 25 a), shows that the Mugar Nano PCC powders were thoroughly integrated into the HDPE matrix. The photos reveal that the Nano PCC particles are dispersed pretty uniformly throughout the polymer matrix, with no major agglomerations or clumps observed. This suggests that the Nano PCC particles were evenly dispersed during the melt blending process and did not experience considerable agglomeration or settling. The particles became more challenging to disperse and maintain in the melt blending process, resulting in larger clusters or agglomerates. This may be due to a variety of factors, such as insufficient mixing, inadequate processing conditions, or poor interfacial adhesion between the particles and polymer matrix. The presence of these large agglomerates can have significant negative impacts on the properties of the resulting lower HDPE/PCC Composite. The agglomerates can act as stress concentrators, leading to weak points in the material and reducing its overall

strength and toughness. The agglomerates can also disrupt the uniformity of the material, leading to variations in properties across different regions of the sample.

CHAPTER FIVE

CONCLUSION

In this study, our primary focus was to synthesize and characterize PCC nanoparticles using a solution method. Additionally, we aimed to investigate the effect of surface modification on PCC nanoparticles and their compatibility with HDPE. Furthermore, we evaluated the impact of tallow surface treatment on the thermal properties of HDPE Nano PCC composites. Moreover, we examined the mechanical and thermal properties of HDPE PCC composites, both with and without organic modification, specifically tallow surface treatment. Our ultimate objective was to determine the optimal conditions for achieving improved properties.

The results of our research demonstrate significant enhancements in the thermal stability and mechanical properties of polymer composites by utilizing both coated and uncoated Mugar PCC Nano powders. These findings provide valuable insights into the potential of PCC nanoparticles as fillers in polymer composites and shed light on the effects of coating them with tallow. Specifically, the coating of PCC nanoparticles with tallow reduced the amount of decomposition during TGA analysis, indicating improved thermal stability. The MCPCC sample exhibited higher ΔH_f and Xc values, indicating improved interfacial adhesion between fillers and the polymer matrix, leading to better filler dispersion and a more ordered crystal lattice.

Additionally, our study revealed significant differences in the particle size distribution between tallow-coated and uncoated PCC nanoparticles. The tallow-coated PCC exhibited increased mean particle size and broader distribution. XRD analysis indicated that Mugar limestone holds potential as a suitable replacement for commercial masterbatch. Notably, the coating surfactant was found to be inert and did not alter the filler's chemistry, rather enhancing its surface properties. Our study emphasized the importance of the weight percentage of PCC in composite materials. Excessive amounts of PCC particles can result in agglomeration and poor dispersion, leading to defects. However, an optimum concentration of PCC particles provided greater reinforcing effects and improved mechanical properties, such as tensile strength. Morphology

testing demonstrated that PCC particles can exhibit both low agglomeration and strong clustering simultaneously. Nevertheless, both MPCC and MCPCC Nano powders exhibited even distribution in the matrix, indicating good dispersion. Overall, our comprehensive findings highlight the potential of Mugar PCC nanopowders and their tallow coating in enhancing the properties of polymer composites. This opens up avenues for the development of advanced materials with improved performance and functionality, contributing to advancements in the field of materials science and engineering. In our study, we also conducted an analysis of the infrared spectra of pure HDPE. The analysis unveiled several characteristic peaks associated with different vibrational modes of the polyethylene chain. The stretching vibrations of C-H bonds in the methylene ($-CH_2-$) groups, bending vibrations of C-H bonds in the methylene ($-CH_2-$) groups, rocking vibrations of the methylene ($-CH_2-$) groups, and bending vibrations of C-H bonds in the methyl ($-CH_3$) groups were all observed. Additionally, out-of-plane bending vibrations of aromatic rings present in additives and impurities within the sample were identified. Based on specific measurements, we observed how the concentration of MPCC fillers influenced the thermal behavior and degree of crystallinity of the HDPE nanocomposites. The higher ΔH_f and Xc values of the MCPCC sample compared to the MPCC samples suggested that the coating improved the interfacial adhesion between the fillers and the polymer matrix, leading to better filler dispersion and a more ordered crystal lattice. Moreover, the lower Xc value of the 40wt% MPCC sample compared to the 20wt% samples indicated a saturation point beyond which the degree of crystallinity did not continue to increase. Furthermore, we investigated the tensile strength and Young's modulus of the HDPE/Nano PCC composites. The addition of Nano PCC increased both the tensile strength and Young's modulus, with varying effects depending on the weight percentage and coating. The results showed that an optimum concentration and tallow coating led to significant improvements in both tensile strength and Young's modulus compared to neat HDPE.

In summary, our study provides a comprehensive understanding of the synthesis and characterization of PCC nanoparticles, the impact of surface modification, and the properties of HDPE PCC composites. These insights contribute to the advancement of materials science and engineering, paving the way for the development of innovative materials with enhanced performance and functionality.

Recommendation

Based on the findings of our study, several research recommendations can be made to further investigate the mechanisms underlying the properties of PCC nanoparticles in polymer composites, as well as to optimize the material design and processing parameters for achieving desired performance.

Firstly, the bimodal distribution observed in DLS of uncoated PCC particles could be caused by several factors, including agglomeration, impurities, or different crystal forms of calcium carbonate. Further investigations are needed to determine the specific mechanisms underlying the bimodal distribution and to optimize the coating process to achieve a narrower and more uniform size distribution of coated particles. Secondly, it is important to consider the effect of impurities or other components in PCC samples on the particle size distribution and properties of the composite. Further research can be conducted to evaluate the impact of these impurities on the particle size distribution and the mechanical properties of the composite. Thirdly, while our study demonstrated that the addition of PCC nanoparticles can improve the mechanical properties of the composite, the specific increase in tensile strength can vary based on processing conditions and material properties. Further research is needed to optimize the material design and processing parameters for achieving the desired mechanical properties of the composite. Finally, it is important to note that achieving the desired mechanical properties of the composite is complex and influenced by various factors. Therefore, further material design and processing optimization may be necessary to achieve the desired performance. Additionally, the optimal weight percentage of PCC may vary based on the specific application and performance requirements of the material. In this case, it appears that 20wt% is the optimal weight percentage for achieving the desired tensile strength of the composite. Further optimization of the material design and processing conditions might be necessary to improve the mechanical properties of the composite at higher PCC weight percentages.

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