CAST COMPOSITE DEVELOPMENT FOR FRACTURE IMMOBILIZATION: AN ALTERNATIVE TO PLASTER AND FIBREGLASS

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A thesis submitted in total fulfillment of the requirements for the degree of Masters in Philosophy

Department of Civil Engineering

University of Moratuwa

Sri Lanka

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ABSTRACT

Plaster of Paris is the most commonly used orthopedic casting material, attributed to its affordability and availability compared to synthetic immobilization materials available in the market. Although widely used in orthopedic casting, plaster has many inherent drawbacks that reduce its durability and patient comfort, especially in long-term immobilization, pediatric, and elderly fracture care.

Degradation upon exposure to water, low mechanical strength, and the heavy weight of the casts have made them less popular compared to synthetic and novel materials. Although plaster casts provide slightly better thermal comfort than their synthetic counterparts, this property still requires improvement.

Through this study, an RHA-modified sustainable plaster cast was developed to fulfill the aim. Since the formula of commercially available orthopedic plaster bandages is a trade secret, this study developed a control mix (commercially available plaster) as the foremost step before selecting a suitable sustainable filler to improve the properties of traditional plaster. RHA was used as a filler material for its low weight, low density, pozzolanic activity enhancement, strength improvement, and thermal insulating properties. The study investigates the microstructure, mechanical properties, and thermal properties of 5%, 10%, and 15% RHA-modified blends made into bandages.

Syngenite formation sites and free water entrapment by RHA particles were observed during the microstructure analysis, which gives rise to variations in the mechanical and thermal characteristics of the samples developed. RHA additions reduced the weight of

the developed plaster by 12.9%–23%. However, setting times increased significantly, with 5% RHA samples increasing the setting time by 7%.

Water absorption marginally reduced in RHA-modified plaster, to approximately 24 times that of the control, but it is still significantly lower compared to waterproof fabric and fiberglass casts. The overall compressive strength increased by 49.2% at 14 days in 10% RHA-modified samples, along with a 6.2% better performance in wet crush strength compared to 5% RHA samples. Performance in tension greatly depends on the properties of the base bandage, with cotton bandages performing poorly in tension. However, 5% RHA-modified bandages showed a 5.8% improvement compared to control samples.

In terms of thermal properties, the heat of hydration reduces compared to the control, proving that RHA-modified bandages release lower heat during hydration. This pertains to the fact that $CaSO_4$ in the mix doesn't undergo adequate hydration in the presence of excess RHA particles. Thermal conductivity and thermal effusivity values also decrease as the RHA percentage increases. Five percent RHA-modified samples show similar thermal conductivity and thermal effusivity values of 0.35 W/mK and 695.2 $W\sqrt{s}/m^2K$, respectively, to the control. A reduction in thermal conductivity reduces the breathability of the cast, causing skin maceration and the buildup of sores. Thus, the developed bandages must possess thermal conductivity above or similar to that of orthopedic plaster.

Based on the conducted experimental analysis, the study concludes that RHA can be used as a sustainable filler to improve the mechanical characteristics of orthopedic plaster, but the thermal performance is not substantially improved. It is feasible to develop a low-cost,

low-$CaSO_4$-containing cast that performs marginally better or almost similar to existing plaster, with less environmental pollution and reduced CO_2 emissions.

Keywords: Rice husk ash, Fracture, Immobilization, Plaster, Sustainability

This thesis is dedicated to;

my late grandfather, for asserting my curiosity ...

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LIST OF ABBREVIATIONS

RHA- Rice Husk Ash

GO- Graphene Oxide

ASTM- American Society for Testing and Materials

MSD- Material Safety Data

PRISMA- Preferred reporting Items for Systematic Reviews and Meta- Analyses

IEEE- Institute of Electrical and Electronics Engineers

CO- Carbon Monoxide

HCN- Hydrogen Cyanide

RTV- Room Temperature Vulcanized

PLA- Poly Lactic Acid

rGO- Reduced Graphene Oxide

DCM- Dichloro Methane

PVA- Poly Vinyl Alcohol

HPMC- Hydroxy Methyl propyl Cellulose

POP- Plaster of Paris

SEM- Scanning Electron Microscopy

BET- Brunauer-Emmett-Teller

CHAPTER 01- INTRODUCTION

1.1 Background

In modern day orthopedics fracture healing, post-operative treatment related to orthopedic trauma and support for structural deformities are conventionally treated by immobilization via casting or splinting.

The process of immobilization, promotes fracture healing by limiting motion at the fracture site, preventing damage to the surrounding soft tissues and the neurovasculature [1]. Limiting movement at the fracture site under rigid stabilization enables direct osteonal remodeling with little to no external callus formation. This is known as direct bone repair under primary healing [2] [3]. Direct bone repair also occurs when a small degree of movement takes place under less rigid interfragmentary stabilization. Here, endochondreal healing at the fracture site or intramembraneous ossification in the periosteum takes place [4]. This condition is generally seen in orthopedic cast or splint immobilization and external fixtures [5]. With higher degrees of interfragmentary movement hypertrophic nonunion can occur at the fracture site which can have deleterious effects on the fractured bone.

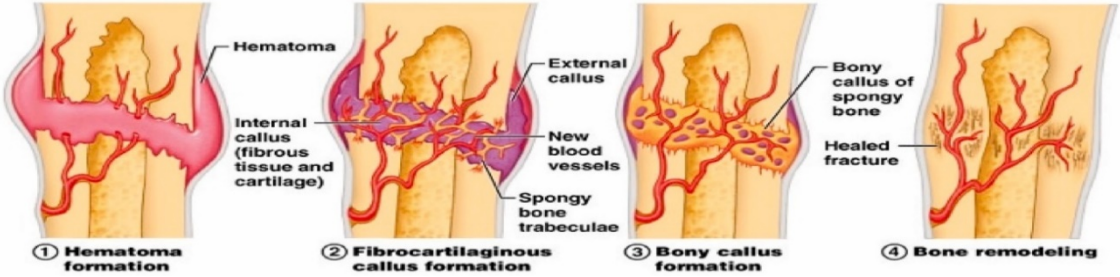

Figure 1: Main stages of the fracture healing process 1) Hematoma formation 2) Fibrocartilaginous callus formation 3) Bony callus formation 4) Bone remodeling

Even though pin fixation through operative procedures are recommended for treatment of unstable severe fractures, cast immobilization is still carried out as a follow up procedure [5] [6]. Generally, the immobilization period for a fracture is 4-6 weeks but this varies with the bone the fracture is located in and the nature of complications [3] [5]. Table 1 refers to the minimum immobilization periods recommended for commonly fractured bones.

Table 1: The most common immobilization periods and the average period for fracture union for commonly fractured bones for cases with no complications [7]

Bone	Most common immobilization periods with no complications (weeks)		Average period for fracture union with no complications (weeks)	
	Adult	Children <10 years	Adult	Children <10 years
Metacarpal	4-6	2-3	6	4-6
Scaphoid	8-12	8-10	15-20	12
Carpal	4-6	2-3	6	4-6
Ulna	4-6	3-4	6-8	4-6
Radius	4-6	3-4	6-8	4-6
Humerus	4-6	3-4	6-8	4-6
Clavicle	4	2-3	4	2-3
Scapula	4	2-3	4	2-3
Ribs	4-6	2-4	4	2-3
Vertebral bones	6-8	4-6	12	6-8
Pelvic bones	6-8	4-6	6-8	4-6
Femur	6-8	4-6	12	6-8
Tibia	6-8	4-6	12	6-8
Talus	6-8	4-6	12	6-8
Calcaneus	6-8	4-6	12	6-8
Phalanges	4-6	2-3	6	4-6

Casting is the preferred technique for long term immobilization of definitive or complex fractures, whereas splinting is preferred for short term immobilization of stable or simple fractures and soft tissue strains and sprains [7] [8]. Due to the rigid circumferential immobilization provided by casts, acute post-injury immobilization that accommodates swelling is carried out by splinting [9] [10]. Casts and splints are also used in correction of congenital deformities associated with the musculoskeletal system such as clubfoot, hip displacements and scoliosis [3] and in diabetic foot care [11].

The first recorded use of orthopedic cast material dates back to the early 3000BC and has evolved to the modern benchmark materials- plaster impregnated bandages and synthetic fiber glass tape [12] [13]. Synthetic cast material such as fiberglass tape and thermoplastics encompass advantages such as superior strength, water resistance and light weight to traditional plaster [14]. These materials have slowly evolved throughout the years registering higher strength, better patient comfort, non-toxicity and more serious concern for the environment.

However, plaster is still the material of choice in many countries due to its availability, ease in application and removal, better conformity to body contours, low irritation and cost effectiveness [15]. Previous studies have reported loosening of the cast due to inflammation at the fracture site, disuse atrophy, poor healing rates, fracture malalignment, pressure sores, compartment syndrome associated soft tissue necrosis, cast burns and inability to treat wounds under the cast as common complications of casting material [1] [15]. These are common to both synthetic and plaster casts but on a wide scale

orthopedics seek to improve the traditional plaster cast to improve cast health and patient comfort due to its advantages over synthetic material.

Cohen and Frillman [16] has shown that organic material is a safer alternative to synthetic fiberglass casting as synthetic casting material are not ecofriendly and register minimal thermal comfort and conformity to body contours. Thus, plaster casts improved with organic additives are of high demand for safe and healthy immobilization.

1.2 Research Significance

Traditional plaster shows better thermal comfort and conformity to body contours than synthetic cast material but complications such as thermal burns, skin irritation and maceration, pressure sores and lower resistance to water degradation are common drawbacks, lowering patient satisfaction and health during immobilization. The development of a new cast by improving the drawbacks in the traditional plaster cast using economical and sustainable agricultural by-product of Rice Husk Ash (RHA) was the main significance of this research.

1.3 Aim

The main aim of this study was to develop a biodegradable composite cast by replacing a percentage of plaster of paris with sustainable agricultural by products such as Rice Husk Ash (RHA), to provide better patient comfort (thermal comfort and cast breathability), lightweight, resistance to water degradation and improved mechanical strength.

1.4 Research Objectives

The objectives of the study were established targeting existing traditional orthopedic plaster of paris casts, which were not up to par in terms of mechanical performance and resistance to water. After analyzing the existing gaps in knowledge, the study was designed to achieve the following objectives;

1. To carry out a systematic literature review to identify gaps and sustainable fillers to improve drawbacks of in orthopedic plaster.
2. To replicate/ develop clinical orthopedic cast material for modification using suitable additives.
3. To conduct testing to identify the most suited material and material properties from the identified fillers to improve mechanical and thermal performance of the control.
4. To conduct a microstructure analysis of the developed product samples.
5. To carry out mechanical and thermal performance analysis on the developed samples.
6. To provide a sustainable alternative to overcome the current drawbacks of the traditional plaster cast, suitable for clinical applications.

1.5 Flow of the Research Study

Figure 2: Steps followed in the research study

1.6 Thesis Outline

The thesis consists of 7 chapters. This section provides a brief introduction to the content of each chapter.

Chapter 1 provides a general introduction to the research covering the concept and importance of fracture immobilization. The immobilization techniques of casting and splinting, the importance of thermal comfort and cast performance are introduced here. Further, the chapter covers the aims and objectives and the research significance laying the foundation for the study.

Chapter 2 provides a systematic literature review carried out on the evolution of casting material, technique of casting, the casting material commonly available for fracture care along with complications associated with casting. The chapter also provides sustainable filler alternatives, including RHA and Graphene Oxide (GO). Thus, highlighting the gaps in knowledge in terms of cast development and thermal comfort enhancement.

Chapter 3 discusses the development of the control mix, eliminating the issues that arose during the optimization the control mix. The chapter investigates the compressive strength alternation when sustainable fillers such as RHA and Graphene Oxide were added to the blends at different compositions. This serves as a preliminary investigation to the study and to optimize the mix design, with most appropriate sustainable filler for further analysis.

Chapter 4 investigates on the selection of RHA replacement percentages that will be subjected to further testing under chapter 5. Compression analysis was carried out on RHA

replacements ranging from 5-30%, to select the most suited percentages of RHA replacement.

Chapter 5 presents the results and analysis of the microstructure analysis, mechanical performance testing and thermal testing of RHA modified samples (5-15%) in comparison to the control. The chapter provides a discussion on each test carried out, providing an elaborate understanding on the performance of each RHA modified sample. The discussion provided under this chapter enables the achievement of the objectives set for the study.

Chapter 6 provides the conclusion from the research including the recommendations for future research following the outcomes of this study. The suitability and feasibility of using RHA as a sustainable filler material in traditional plaster casts to achieve mechanical strength and thermal comfort during cast layup is conclusively drawn under this chapter. Thus, providing a clear pathway into developing sustainable orthopedic casts for pediatric and elderly fracture care.

1.7 List of Publications

The following journal articles were published and submitted based on this research.

1. C. Ekanayake, J. C. P. H. Gamage, P. Mendis and P. Weerasinghe, "Revolution in orthopedic immobilization materials: A comprehensive review," *Heliyon,* vol. 9, no. 3, p. e13640, 2023. https://doi.org/10.1016/j.heliyon.2023.e13640

2. C. Ekanayake, J. Gamage, P. Mendis and P. Weerasinghe, "Sustainable fillers to address inherent drawbacks of orthopedic plaster," in *ICSBE*, Kandy, 2022.

CHAPTER 02- LITERATURE REVIEW

2.1 Introduction

This chapter presents a systematic literature review analyzing the existing state of literature, pertaining to fracture immobilization. It gives a detailed exploration into fracture casting material evolution throughout the years and the complications associated with casting.

Further the chapter provides an overview on the applicability of RHA and GO as additives to plaster and $CaSO_4$ based systems, analyzing the performance enhancement in such systems. This provides insight as to why RHA is a suitable modifier for plaster-based cast performance and thermal comfort enhancement.

Paper 01

2.2 Material Evolution and Technique of Casting

2.2.1 Evolution of Casting and Splinting

According to the Edwin Smith's surgical papyrus, the earliest use of fracture immobilization techniques dates back to 3000 BC, where splints designed from sticks and palm fiber bandages and linen were found from prehistoric mummies [17]. Hippocrates had documented the importance of splinting and use of bandages stiffened with wax, lard or resin and multiple bandage layers for fracture care. It is manuscripted that linen glued together with plaster and splints made of bamboo were in use from 600 BC to 600AD [8] [14]. Although plaster came to existence with the development of art plaster frescoes

during the Roman Empire, it was not used for medical care at the time [18]. “Plaster of Paris” (POP) was introduced as a replacement for lime used in bandage stiffening in 1798 [17].

During the battle of Borodino, Dominique Jean Larrey (1766 to 1842) applied a rigid dressing to a wounded infantryman following an amputation. Three months later, upon the removal of the dressing, the residual limb had healed. This concluded that the rigid dressing immobilization accelerated fracture healing [13-15] [17]. With the acceptance of limb immobilization for fracture healing, the first use of Plaster of Paris as a cast was carried out at the beginning of the 19th century in Europe. They poured Plaster of Paris around fractured limbs encased in a wooden construct, which was known as ***plâtre coulé***. The technique of plâtre coulé has refined patients to one place during the entire healing process due to the weight of the cast [13,14]. The first Plaster of Paris bandage was invented in 1852 by A.Mathijsen, a medical officer of the Dutch army. Mathijsen manually rubbed Plaster of Paris on coarse cotton bandages in cast preparation, a method similar to the plaster impregnated bandages used today [18,19]. Since the Crimean war (1854-1856) Plaster of Paris (POP) bandages have been extensively used in fracture immobilization, through which the modern fracture immobilization technique emerged [2] [19]. The early plaster bandages were made by soaking woven bandages in freshly prepared plaster by the hospital staff. The first commercially manufactured plaster bandages were available in Germany during the early 1930s, where plaster was mixed with minor quantities of volatile liquids on soft cloth bandages [2] [13].During the 1950s resin-based plasters were introduced along with high temperature thermoplastic material

gaining popularity in splinting. Low-temperature thermoplastics were introduced during the 1960s replacing these high temperature thermoplastics and the 1970s mark the first generation of synthetic casts with the 1980s demarking the second generation of synthetic casts. Generation 2 synthetic casts were commercialized with improved conformability and better handling ability with low tack Polyurethane (PU) resins. Since the 1990s, the third generation of synthetic casts has evolved with materials such as high strength polyester, registering enhanced conformability and elasticity (Refer Figure 3).

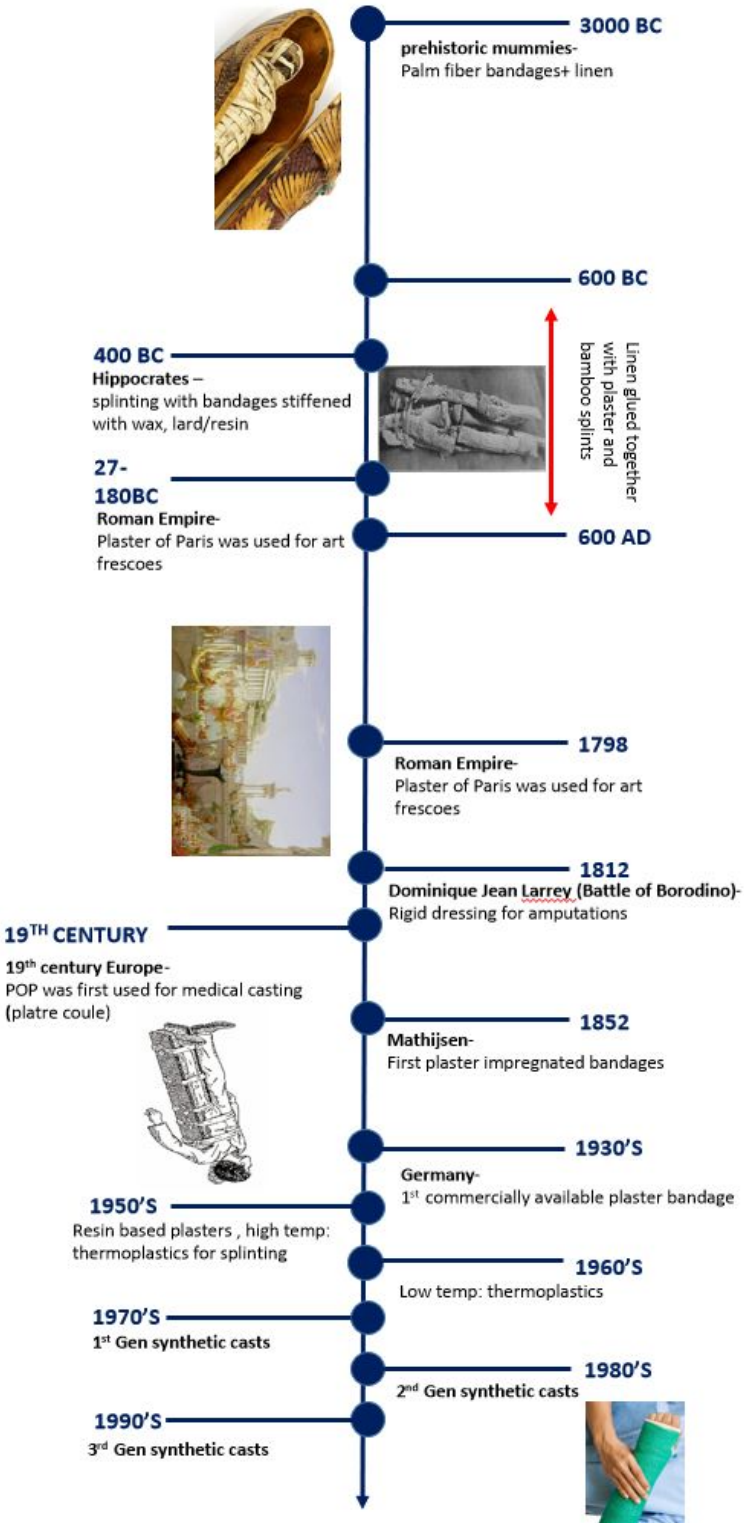

Figure 3:Timeline of evolution of orthopedic immobilization material developed by the author

2.2.2 Cast Application and Techniques

Prior to immobilization, it is important to have a clear idea of the neurovasculature and the surrounding anatomy. The skin must be observed for any inflammation, lesions or soft tissue injuries [20, 21]. According to Smeltzer et al. assessing the five **P**s: pain, pallor, pulselessness, paresthesia and paralysis is mandatory [21, 22] to minimize cast complications. In high risk patient groups such as pediatric patients, multi-trauma patients, comatose patients, patients under anesthesia and patients with developmental disorders where effective communication is impassable, certain casting material and techniques are recommended to avoid morbidity. However, when the fracture site is prone to swelling and bleeding, temporary immobilization using a splint is recommended [1].

To ensure proper fracture alignment and minimal complications, cast application has to be carried out by practiced orthopedic technicians or medical practitioners. The proper application technique includes the placement of the limb in the desired position for comfort. Casts are applied as a total contact cast, which is directly applied to the skin, or applied over a stockinette sleeve and layers of padding [21][23].

The application of plaster casts is technically simple compared to other cast materials [20]. Initially, a stockinette is applied to the skin followed by padding wrap for patient comfort. Practitioners can slit the padding along the entire length of the limb and apply a layer over the slit about ¾ the circumference, to accommodate any post traumatic swelling. The ends of the stockinette sleeve can be folded back over the padding to provide cushioned ends and better ventilation into the cast [23] [25,26]. Next, the plaster / synthetic tape bandages are then dipped in tepid water. The ideal dip water temperature is maintained between 32-

39 °C [27, 28]. It is important to change the dip water after each application to remove plaster/ synthetic resin deposits that can increase the dip water temperature. Practitioners are recommended to use gloves when using synthetic cast material to avoid exfoliative dermatitis and skin irritation [21].

Plaster/synthetic bandages are stretch-relaxed and laid up not pulled. As casts are generally applied over a layer of padding, the use of a very thick layer of padding can weaken the plaster. An ideal cast is required to be thin and strong. Generally, 7 to 8 layers of bandage are used in plaster casts and 3-4 layers of synthetic tape in a fiberglass and other synthetic casts [22]. Rubbing each layer before the next layup ensures bonding between layers for stronger and lighter casts [21] [23] [26]. According to Luck [19] rubbing under pressure can damage the underlying neurovasculature hence adequate force has to be applied during the process. Alternatives to the general application process of fiberglass tape was discussed by Smith et al. [21], where they applied fiberglass tape without water immersion and used a water-based gel on fiberglass tape to activate the resins.

As plaster and fiberglass bandages are dipped in tepid water, fast dipping and aggressive squeezing off of the water can result in making the casts hotter due to water inadequacy, resulting in cast burns. Luck [19] states that longer soaking times (> 4 mins) associated with higher dip water temperatures (> 95^{o}F) results in a steady decline of the compressive strength of plaster casts. Hence, dip water temperature and soaking time must be properly managed by technicians for stronger and safer cast application.

For proper immobilization, the casts must completely dry. This depends on the cast thickness and the material used. The complete drying of a plaster cast takes 36 -72 hours and can become weight bearing only after about 48 hours in the case of long leg casts and hip spica casts. However, the curing time for fiberglass and other synthetic cast material is 25-30 mins and can immediately bear weight upon hardening.

As pointed out under aims and objectives, the selection of the cast material is based on the application, length of immobilization, material availability and cost concerns.

2.3 Methods

To fulfill the aim of this study, the authors applied a five- step method (Refer Figure.3)

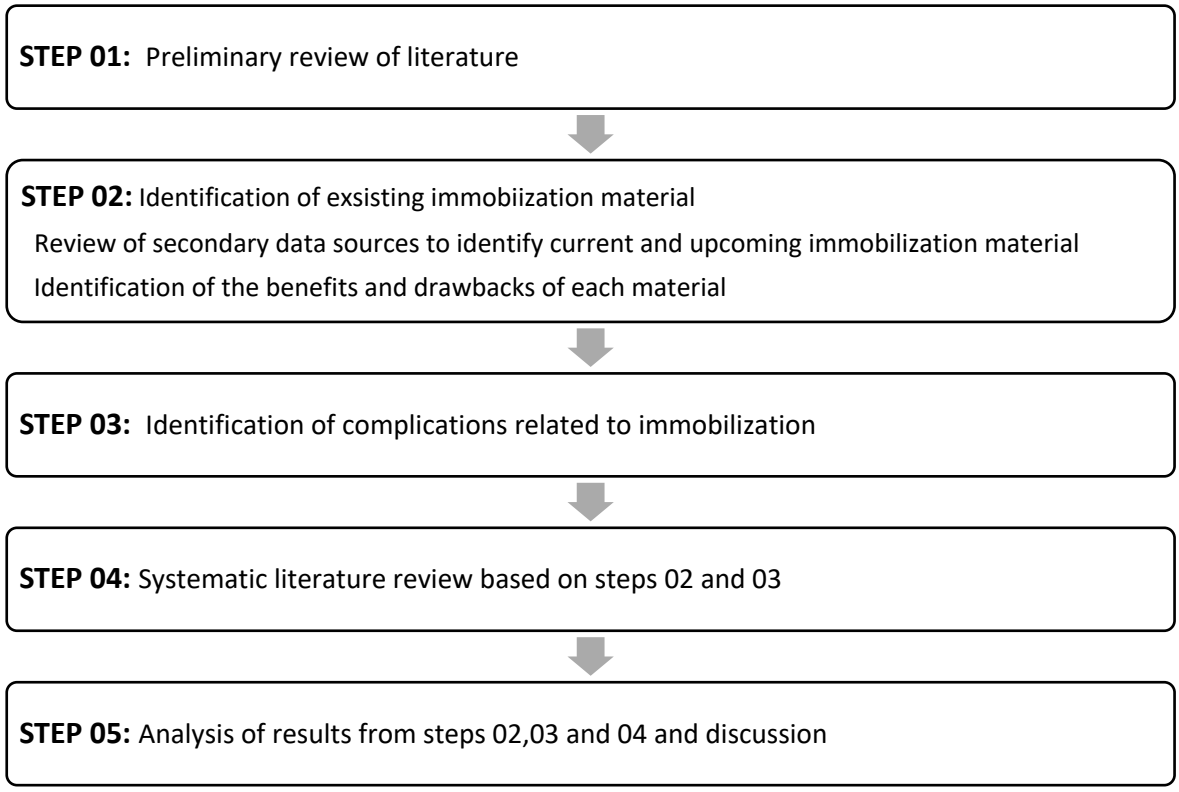

Figure 4: Steps followed for the systematic literature survey

Under step 1, the authors carried out a preliminary review to understand the evolution of the immobilization material, their history, techniques in cast application, to build up the basis for the review. Precise identification of terminology and techniques of casting and splinting was carried out. The detailed outcomes of the preliminary review are presented under Section 2. The authors have identified that the technique of fracture immobilization dates back to the early 3000 BC, while understanding the underlying anatomy and accounting for the 4Ps is important before the application of the casts and splints.

Based on the results obtained in Step 1, the existing immobilization material were identified through secondary data sources. The secondary data sources used under Step 2 are, technical papers, journal articles, medical journals, MSDs, manufacturer's websites and reports and standard medical articles and books. The nature of the immobilization material along with their benefits and drawbacks are identified under Step 2.

Under Step 3, the complications associated with immobilization is broadly discussed. This provides a complete understanding of the most critical complications that immobilization is associated with. Similar to Step 2, the data was gathered through secondary data sources inclusive of patient feedback forms.

Step 4 provides a systematic review of the journal papers selected in Steps 2and 3. This systematic literature review was carried out via the "Preferred reporting Items for Systematic Reviews and Meta-Analyses (PRISMA)" that provides a higher transparency into the reported systematic review.

The search for literature was done using abstract and citation databases such as PubMed, Medline, Science Direct, Scopus and IEEE Xplore digital Library for Peer-reviewed articles published from 1980-2022. This time frame was decided as studies on plaster modifications were carried out earlier on and a comprehensive understanding on gypsum plaster casts is crucial to this review. The literature search comprised of fields “article title”;”abstract”;and “keywords”. The selection of the keywords was done through the preliminary examination of accessible literature and former reviews carried out on related titles and through the identification of recurring themes. The authors agreed upon a set of keywords to increase the probability of identifying of all relevant publications. The Boolean operators AND and OR were used in the syntax. The following search terms were used for the query: (“casting*” or “splinting*”) and (“immobilization*” or (“plaster” and “gypsum”) or (“synthetic” and “casting” and “material”)) and ((“fibreglass” or “hybrid” or “polyester” or “polyurethane” or “thermoplastics” or “silicone” or “rubber”) or (“casting” or “orthopedic” or “novel”) or (“new” or “composites” or “bioplastic” or “PLA” or “wood” or “sustainable” or “flammability” or “radiolucency” or “comfort” or biodegradable”)) or ((“thermal” and “burns” or “pressure” and “sores” or “thrombosis” or “swelling” or “hemotoma”) or (“cast” and“saw” and “burns”) or (“venous” and“congestion”) (“casting” and “complications”)).

The initial database searches generated 948 publications, and 25 additional studies were sought from reference lists of retrieved studies and review articles (Fig. 3). Following the removal of duplicates, records published before 1980, and irrelevant citations based on fast screening, 135 publications were further assessed for selection. Given the study scope

and data acquisition requirements, original studies were eligible to be included in this review when: 1) the immobilization material was examined and analyzed; 2) the complications associated with immobilization was discussed. A total of 95 studies met all the selection criteria and were included in the final data synthesis of the review. The AI assisted tool, Research Rabbit was used to search more refined papers with higher relevance to be added to the 95 papers already chosen through the selection criteria. Relevant documents were collected and organized in EndNote 20. Lastly, the findings were analyzed and discussed under Step 5.

PRISMA flowchart is given in Fig. 5.

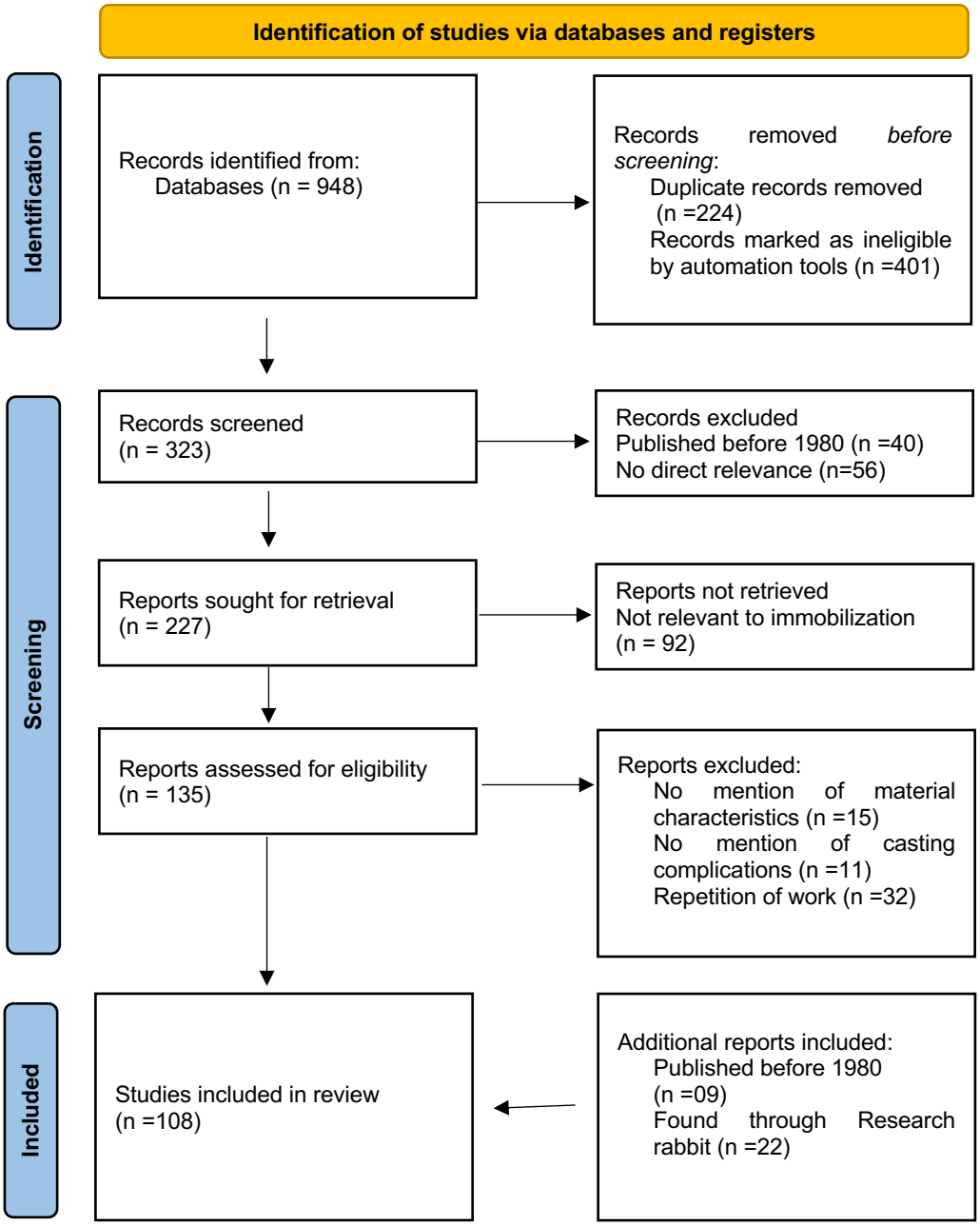

Figure 5: PRISMA Flowchart

2.4 Findings

Based on the findings a detailed analysis of the existing orthopedic immobilization material and the complications associated with immobilization are comprehensively analyzed.

2.4.1 Existing orthopedic immobilization material

2.4.1.1 Plaster of Paris

Plaster of Paris (POP) is the most popularly used casting and splinting material to this date. Casts and splints fabricated from Plaster is used not only for immobilization of fractures but also in the correction of bone related deformities such as clubfoot and as a support for sprained ligaments and inflamed or infected soft tissues [13].

To refine Plaster of Paris, gypsum is heated to about 120° C, which removes most of the water from the crystals resulting in a powdery residue [23].

$$2(CaSO_4.2H_2O) \rightleftharpoons (CaSO_4)2.H_2O + 3H_2O \quad (1)$$

Plaster, promptly absorbs water and undergo crystallization in a rapid exothermic reaction. The complete reaction happens in two steps. Initially there is a slight expansion of volume during the setting stage and becomes a porous mass at the hardening stage [13].

When observed under a microscope, the rapid forming crystals during the setting stage, tightly interlock resulting in good mechanical strength gain and rigidity. For proper crystal interlocking, immobility of the plaster cast is essential. This is called "**The Critical Point**", where immobility of the plaster is imperious for it to set properly and become

rigid for ultimate strength gain. According to Luck [19], plaster casts that undergo bending after reaching the critical point, showed a 77% reduction of overall strength.

Post crystallization, the excess water evaporates from the surface giving plaster a grainy appearance. The setting time of POP casts depend on the additives [24] used and manufacturers generally provide the cast setting times of the product [17]. Commercially available plaster bandages comprise approximately 85% Calcium Sulphate by weight and binders which enable strong adhesion of the plaster to the bleached cotton fabric. According to Burrows and Milne [25] , plaster detaches from the cotton bandage when wetted. To enable strong cohesion of the plaster to the bandage, additives such as hydroxypropylmethylcellulose (dry powder) is added. The composition of the additives is to be maintained at 0.1% to 5% by weight to preserve the properties of plaster. To avoid dry plaster detaching from the bandage, a fine mist of propylene glycol is uniformly sprayed on to the plaster bandages [25]. According to Abbood et al. [26], additives such as Tree Glue Powder (TGP) and Polyvinyl Acetate (PVA) have been used to improve the setting time of plaster casts.

Plaster casts show steady strength gain during the first three to six days post application as more and more excess water comes to the surface to evaporate. It is highly recommended to dry plaster casts by natural methods, as artificially generated heat can cause thermal damage to the patient. Upon complete drying, plaster gains porosity, thus allowing the moisture to be absorbed from the underlying skin. The “wick effect” created

due to micro cracking also adds to the vapor permeability of plaster. Perspiration, blood and puss are readily absorbed by plaster casts, thus preventing skin maceration [27].

Plaster encompasses many advantages such as availability and low cost, making it the standard casting material. Plaster has a superior ability to confirm to body contours than synthetic material [34,35]. Hence, it is highly recommended when casting extremities. The increased conformity of plaster provides a low tendency to create pressure areas than other materials and less shear, reducing skin irritation. Plaster retains body heat, creating a gentle and neutral warmth with a low probability of resulting in skin lesions during long term immobilization [17].

Practically, plaster is brittle and has poor mechanical properties compared to its synthetic alternatives. Hence, the addition of additives like Calcium Oxide, Ferric Oxide and Gum Arabic significantly improves abrasion resistance, tensile, compressive and transverse strength and reduces the possibility of material fracture upon hardening [29] [36-38]. According to Mihalko et al. [28] plaster casts show bilinear characteristics as the plaster and the gauze bandage behaves as two separate units when subjected to tensile testing. Mechanical testing carried out by Agisparayan et al. [29] shows that plaster is susceptible to degradation under impact forces and can only absorb 1.222 J of impact energy when subjected to Charpy impact testing. Although additives have been effective in reducing plaster setting times, lengthy setting times is still a major drawback of plaster casts in comparison to synthetic material. The low fatigue strength of plaster results in increased cast breakage during weight bearing and movement [30] in long leg and hip spica casts.

Another major drawback of plaster is its fast degradation when wetted, limiting the ability of patients to bathe and swim while fitted to the cast. Hence, waterproofing plaster casts is a major issue during long term immobilization.

The high mineral content and crystallization of plaster, attenuates and scatters x-rays [31], resulting in a thick radiopaque layer. This makes it difficult to carry out proper x-ray diagnosis of the underlying bone without cast removal [32].

Today gypsona impregnated leno-weave gauze bandages are popularly used than traditional plaster. Gypsona is plaster of paris with minimal additives with a much creamier consistency, but traditional plaster casts are more durable and water resistant than their gypsona alternatives [33]. According to Rowley et al. [34] the nature of the bandage weave has no significant impact on the durability and strength of the cast. Newer variations of plaster such as resin augmented plaster has considerable durability and higher water resistance [34].

2.4.1.2 Synthetic cast material

Overcoming the drawbacks of the traditional plaster casts, new synthetic cast materials have evolved. These mainly include polyester/cotton knit, fiberglass and thermoplastic [35] cast material. Studies have shown that many water-activated synthetic materials decrease in stiffness following water immersion (<53%) but regained up to 90% within 24 h [27]. Synthetic material that undergo exothermic reaction [2] upon water immersion record very high temperature levels between the initial 7-10 minutes, which can result in

first degree burns. Hence, caution is necessary when applying synthetic casts on fresh fractures where swelling is highly likely.

Many synthetic casts are porous. Therefore, it allows air circulation through the cast reducing the risk of skin maceration. Synthetic materials are better alternatives to traditional plaster in water resistance and radiolucency. Some studies [30] [36] have shown that patients prefer synthetic casts to plaster due to better patient comfort, lightweight and superior mechanical properties.

2.4.1.2.1 Fiberglass casts

Today, fiberglass is one of the most commonly used materials for casting and splinting in developed countries. According to Lisa [37] the use of fiberglass casts dates back to the 1970s. The earliest was knitted Fiberglass bandages impregnated with a light-activated resin, which was recorded as the first synthetic cast material to be developed. The earliest fiberglass bandages hardened upon exposure to UV light forming a hard cast. In 1978, the first water activated synthetic fiberglass bandages were introduced by Cutter Biomedical. Dyncast XR (Smith and Nephew), Delta-Lite 'S' (Johnson and Johnson), Ortho tape, Scotch cast, Scotchflex (3M), and Zim-flex are some of the widely used commercial fiberglass brands [43] [45] [48,49]. Apart from the Urethane pre-polymer, some commercial brands such as Delta- Lite 'S' (Johnson and Johnson) and Scotchcast Plus (3M) include additives such as Silicone [36] [38].

Modern fiberglass tape is impregnated with polyurethane or a polyurethane resin. Stretch-relaxed fiberglass tape is dipped in water at 20- 25 ° C to activate the resin and applied in

the same manner as plaster casts (116). It is best to carry out moulding and conforming after 3-6 minutes of application before hardening. Some studies [22] [39] have shown that temperatures above 49°C beneath the cast over an extended period of time can cause superficial thermal injury. Hence, extra caution is required when applying extra fast setting and thicker casts with dip water temperatures above 32° C.

The main advantage of fiberglass casts is their lightweight (i.e. 1/3 the weight of plaster casts) [3], water resistance, durability, quicker setting times and strength (2-3 times stronger than plaster). Load displacement curves for fiberglass tape shows linear characteristics [40] concluding that the resin and bandage act as one unit with yield strengths twice that of plaster [28]. Generally, fiberglass bandages are stronger and rigid across the bandage than along the length [27]. According to Rowley et al. [34] the fast curing nature of fiberglass allows weight bearing earlier on. They further state that in fiberglass and resin bandages, the type of the weave shows a significant impact on the lamination and flexibility of the end product. This is due to the nature of the weave aiding cross –bonding between molecules on either side of the laminate. According to Martin et al. [38] the differences in the mechanical strength and performance among the many varieties of fiberglass tapes mainly vary due to the anisotropy of the material caused by irregular resin distribution along the tapes.

Generally, fiberglass is a porous material hence it reduces the risk of skin related issues making it suitable for long term immobilization [3]. Past studies have proven that fiberglass casts can withstand water degradation [52,53] and can be wetted during bathing,

but the drying process has to be carried out with caution adhering to provided instructions. Clinical trials conducted by Inglis et al. [30] recorded that patients treated with fiberglass casts reported no skin complications after swimming and bathing. According to Lisa [37] it takes approximately an hour to completely dry the cast. Commercially available fiberglass casting tape comes in different colors which provide the user with a cosmetic advantage apart from rigid fracture immobilization.

Flammability tests carried out by Wytch et al. [27] [31] show that fiberglass casts have a low ignition temperature and a heat transfer rate of 29, although polyurethane used in them is highly flammable. Although other PU resin casts burn easily, the fiberglass in PU coated fiberglass bandages causes a heat sink effect which reduces the local temperature. Thus, fiberglass casts impose a low to moderate risk when operating near naked flames. According to [34], urethane pre-polymer impregnated fiberglass bandages have higher radiolucency than plaster. Radiographic assessments carried out by Wytch et al. [32], show that fiberglass, although radiolucent than plaster, records varying interference patterns based on the mesh pattern of the bandage. Also, the level of attenuation increased with the increasing number of layers.

Unlike plaster casts which can be handled or moulded without the requirement of gloves, technicians require gloves during application and moulding of fiberglass casts [33]. This is mainly due to the adherence of the water activated resin to the skin [25] [46] which facilitates free isocyanate groups to come in contact with the applicator's skin [31], causing exfoliative dermatitis. The vapor permeability of fiberglass-polyurethane

bandages is much less compared to the cotton and polyester alternatives available. This makes them unsuitable in the presence of wounds on the skin surface and can result in skin maceration [27].

There is growing concern regarding airborne fiberglass particles and dust during cast removal using cast saws. Past Studies have identified that isocyanates in synthetic cast material can cause occupational asthma, coughing and laryngospasm [27] [31]. Hence, modern cast saws are equipped with a vacuum to absorb the airborne fiberglass dust.

In order to tackle latex sensitivity of pediatric patients and patients with higher skin sensitivity, newer latex-free casts such as Delta-cast and Flashcast-Elite are available. These comprise of a polyester substrate with extensible yarn encompassing all the properties of the fiberglass casts but with an improved finish and conformability with no fiberglass dust generation during removal.

2.4.1.2.2 Plaster - Fiberglass Hybrid

Previous studies have shown that fiberglass and plaster possess qualities that are placed far apart in the spectrum of parameters analyzed for a good fracture casting material [40] [52] [56,57]. To achieve a feasible solution, Terry and Mark designed a hybrid cast combining traditional plaster and fiberglass, thus optimizing the advantages of both materials.

Plaster provides better conformity, economic feasibility and patient comfort while fiberglass provides durability, strength and significantly reduces the weight of the resulting cast [41].

Terry and Mark's hybrid cast consists of two layers of plaster bandage overlaid by two layers of Fiberglass tape. An improved version of the hybrid cast was designed by Agisparayan et al. [29] where 4 layers of fiberglass bandages were laid over 4 layers of plaster placed over a layer of cotton padding. According to Kelly [42] fiberglass tape was used as a reinforcement to enhance durability and water permeability of plaster casts, resulting in a plaster-fiberglass hybrid.

According to Terry and Mark the hybrid cast is more stable and registered fewer fatigue lines compared to traditional plaster when subjected to a Tukey test [41]. Charpy impact testing carried out by Agisparayan et al. [29] showed that plaster is brittle hence fractures with no significant deformation, while fiberglass underwent ductile failure due to fiber rupture. The hybrid cast was able to withstand moderate impact energy and failed under both brittle failure from the inner plaster layers and fiber rupture from the outer fiberglass layers [29]. This proves that the impact forces are predominantly borne by the outer fiberglass tapes before being transferred to the plaster layers beneath. This study showed that no delamination between the two materials were observed at failure. This ensures that the toughness and the impact resistance of the hybrid cast is superior to plaster. However, on removal with a cast saw, the fiberglass tapes completely separate from the underlying

plaster suggesting that no significant chemical bond occurs between the two mediums [42].

The hybrid bandages could withstand 15 to 25 times more flexural loads than plaster, before undergoing failure. This was almost similar to the flexural strength of fiberglass with a flexural modulus 3.8-4 times higher than plaster, mainly due to a majority of the flexural loads being borne by the outermost fiberglass layers. Thus, making it suitable for fractures near joints and areas experiencing high stress [29]. The indentation hardness of the hybrid bandages showed almost equal values to that of fiberglass. The main reason being the mesh-like surface of the knitted fiberglass tape of the hybrid cast [29].

According to Charles and Yen [43], the hybrid casts constructed of 2 inner plaster layers and a single fiberglass layer were two times stronger than plaster when subjected to 3-point bending and shear tests. The shear strength of the plaster-fiberglass interface was higher by a factor of 3 than the 3-point bending strength of the construct. The hybrid constructs weighed 14% less than plaster but 42% more than fiberglass. In terms of cost comparison hybrid constructs were 2.5 times the cost of plaster and half the cost of fiberglass.

Although the hybrid alternative is not tough as fiberglass tape, it aids to overcome the brittleness and low impact resistance of plaster and provides a cheaper and sustainable alternative to a fully fiberglass cast [29] [43], with the added comfort of plaster. Studies have shown the hybrid cast to be suitable for extremity casting, especially lower extremity where plaster casts fail upon weight bearing and fatigue [56,57].

2.4.1.2.3 Polyester-Polyurethane and other Polyurethane impregnated casts

Apart from fiberglass, advances in the polymer industry have put forth fabric material impregnated with polyurethane resin such as polyurethane-polyester. These materials are gaining popularity due to their low cost, availability, high-strength-to-weight ratio, extensibility and low hygroscopicity [27] [44].

Delta cast conformable is an excellent example for a polyester- PU cast [2]. Other commercially available polyester-polyurethane resin bandages go by the names of Dyncast, Deltacast plus, Deltacast®, Baycast etc. These follow similar activation by immersion in water as plaster and fiberglass bandages.

All polyurethane impregnated bandages use similar resins, which in the presence of a catalyst combines di-isocyanate with polyol to form a prepolymer urethane (PU) resin [44].The Urethane prepolymer when combined with water liberates heat and carbon dioxide forming crude polyurethane.

$$\textit{Prepolymer (with isocyanate end groups)} + H_2O = \textit{polyurethane polymer} + CO_2 \quad (2)$$

Unlike fiberglass casts, the prepolymer contains negligible quantities of free di-isocyanate due to the presence of excess polyol added during the manufacturing process. Chemicals such as stabilizers remove water molecules to avoid curing during storage and anti-foaming agents remove carbon dioxide liberated following water immersion [27]. Although Polyols and antifoaming agents added are non-toxic, the catalysts and stabilizers

show a strong irritant and toxic nature even in very small quantities (<1-2%). Therefore, it requires immersion in excess water.

The application process of PU resin bandages is similar to that of plaster but manufacturer's instructions are to be closely followed. Polyurethane resins are sticky and adhere to the skin. Hence, it requires the use of gloves and are difficult to handle. PU resins can cause skin irritation after prolonged exposure. New low-tack resins with added surfactants to reduce the surface tension are currently commercialized. This reduces very high adherence and promotes ease in handling and application.

Polyurethane-Polyester casts record higher elongation and diametral compression strength in comparison to polyurethane-fiberglass casts. The tack free time and setting time can be effectively reduced by increasing the NCO/OH molar ratio in the prepolymer. This simultaneously results in an increase in diametral compression strength, although increasing the molecular weight in polyol in PU resins resulted in contrasting results [44]. Clinical studies evaluating the mechanical properties of casting material show that PU resin bandages are weak across the width of the bandage making them weaker candidates for load bearing casts. In terms of conformity and moldability Polyester-PU resin casts were rated lower than plaster [45].

Due to the elastic and flexible nature of polyester and polypropylene casts, these record very low cast breakages when compared to traditional plaster. Petty and Wardman [46] concluded that patients fitted to polyesters casts benefit from the flexibility of the cast in attending to their day to day activities. In contrast hardened PU bandages can result in

rough surfaces and sharp edges. These can get caught in patient's clothing and cause discomfort in day to day activities [2]. Although performance of cotton base PU resin bandages is not a satisfactory improvement on plaster bandages, the cotton base provides lower dead weight [47].

Radio attenuation assessments carried out by Wytch et al. [32] concludes that polyurethane resin on knitted polyester bandages shows very low x-ray attenuation, ensuring better radio diagnostics of the underlying bone. Hence, polyester-polyurethane casts show superior radiolucency to that of fiberglass tape and POP and requires no cast replacement [2] [47].

Polyester- polyurethane and polypropylene-polyurethane bandages are extremely flammable (ignition time 6s and 45s respectively), thus making them a potential fire hazard [42] [62]. Although the heat transfer rate is adequate enough to alert the wearer to remove from the proximity, it is cautious to avoid cast exposure to naked flames [48]. Especially polyester casts that have a heat transfer rate of 18. PU impregnated bandages liberate Carbon Monoxide (CO) and Hydrogen Cyanide (HCN) upon ignition [31]. However, the concentrations of these gases are low and unlikely to cause respiratory difficulties to the wearer.

Clinical studies show that PU resin casts have recorded skin sensitization in patients. Similar to fiberglass -PU resin bandages, these too use isocyanates and other irritant chemical additives making them toxic and hazardous. In comparison to fiberglass, these produce lower amounts of dust during cast removal. Thus, the risk of work- related asthma

is lower in other PU resin bandages than fiberglass-PU tape [2] [42]. Further, the non-biodegradable nature of PU resin casts is an environmental burden that results in landfills and toxin leakage to ground water.

2.4.1.2.4 Thermoplastics

Thermoplastic materials are formable when heated and acquire rigidity when cooled [49]. These are widely used in splinting than casting. Thermoplastic casts are made out of an open-weave fabric comprising of a linear thermoplastic polyester polymer. Some thermoplastic and polyester composite casts such as the commercially available product Hexcelite NS contains a thermoplastic linear polyester polymer with an inorganic filler on a cotton base [24] [48].

Fillers, elastomers and resins like polycaprolactone are added to thermoplastics to increase memory, stiffness, durability and moldability, while inorganic fillers improve the rate of cooling and heating [50]. The cast bandages have to be preheated in water at 170°C before application. This makes them soft and moldable for conformity. Low temperature softening thermoplastics are mainly used in casting and splinting to avoid thermal damage to the patient during the casting process [50]. These thermoplastics activate when immersed in hot water at 70-75°C for 1-2 mins. They have a low curing time of 3 mins and can bear weight after 15 mins [51]. The application procedure of thermoplastic casts is similar to that of plaster but they offer much cleaner working conditions compared to plaster casting [2]. Casts fabricated from thermoplastics can be reheated at relatively low

temperatures [50] for remoulding to alter the cast position without removal, enhancing their cost benefit.

In testing for moldability and durability of low temperature thermoplastics, Breger-Lee and Buford [50] concluded that thermoplastics show 0% to 86% permanent deformation based on their ability to retain elasticity during load cycling. Thermoplastics with higher elastomeric properties showed the least deformation while those with higher plasticity undergo large viscous energy dissipation. Low temperature thermoplastics provide longer working times and can be stretched to the required length when heated but returns to the original dimensions upon cooling due to elastic memory [49]. Hence, enhancement of low temperature thermoplastics with elastomers enables flexibility in casts and splints. A majority of low temperature thermoplastics can be easily cut with a pair of scissors while the material is warm and be conferred into the desired shape. However, stiffer thermoplastics sometimes require a coping saw.

Clinical studies carried out by Jø et al. [52] show that bandage comfort was significantly higher in Hexcelite than plaster casts when used for below-knee walking casts. Some past studies have shown that the weight bearing ability of a majority of thermoplastic casts is lower than that of their fiberglass alternatives [48, 49].

Although thermoplastic casts are lightweight and have good water tolerance, they bear many drawbacks. The temperature required to activate a thermoplastic cast material is high as 70-80°C and can cause thermal damage to the technician as well as the patient. Shorter moulding durations are available as the casts harden while cooling. Hence, it

demands special training for proper application [64, 65]. These have low conformity compared to plaster casts and can result in sharp prominences and wrinkling of the material that can cause pressure sores [65, 66]. The material cost is significantly higher than plaster but lower than or equal to that of fiberglass [31].

Many thermoplastic materials are radiolucent but the underlying meshwork appears in the x-ray images making it difficult to clearly identify fracture lines [32] [47]. The material expense and its drawbacks have made it less popular in fracture immobilization [20] in developing countries and for long term immobilization.

2.4.1.2.5 Silicone rubber

Silicone rubber- Room Temperature Vulcanizing (RTV) is widely used in splints and casting in sport related injuries where more flexibility with adequate immobilization is required [67, 68]. These casts and splints are generally used for upper extremity injuries such as wrist, thumb and the carpal navicular.

Bassett III et al. [53] was the first to describe a cast made of medical gauze impregnated with RTV Silicone Rubber. A similar splint was tested by DeCarlo et al. [54] with added reinforcement such as aluminum, concluding that the hardness and flexibility of Silicone rubber can be controlled enabling a thin durable cast. According to Bassett III et al. [53] the degree of immobilization depends on the amount of silicone and the supporting materials used.

In preparation of Silicone Rubber, catalysts are mixed to provide curing times of 2-4 hours. Further, Urethane foam padding is used as an underlying material in Silicone rubber splints [55]. Bergfled et al. [56] using a splint constructed of Silicone rubber (RTV 700), curing agent -Beta 2 red, medical gauze and Ensolite foam between the layers of silicone concluded that the required rigidity and shock absorbing qualities were present in Silicone rubber splints making them adequate candidates for sport related injuries.

According to Bassett III et al. [53] silicone rubber although not hard as fiberglass or plaster is rigid enough for short term stabilization for injured athletes. Silicone rubber results in soft casts but when combined with the padding under layer has superior shock absorbing qualities than their alternatives [54]. The non-porous nature of silicone rubber allows them to be used only for short term casts and splints.

2.4.1.2.6 Other cast material

Synthetic cast materials pose a wide array of environmental and health risks. Hence, ecofriendly sustainable alternatives are emerging [57]. These substitutes are developed to overcome the issues faced by traditional plaster while providing adequate immobilization at the fracture site.

2.4.1.2.6.1 Woodcast

Modern day synthetic cast material contains Methylene Diphenyl Diisocyanate (MDI) which has shown links to occupational asthma and toxicity [58]. Hence, Onbone Oy, Finland has developed a new wood-plastic composite material, Woodcast. Woodcast is

fabricated from a biodegradable thermoplastic polymer (bio plastic) and woodchips [59]. It is a fabric like material made from fine-chipped woodchips acquired mainly from the Finnish aspen or spruce trees. The fine-chipped wood is certified for medical purposes [60].This mass of fine-chipped wood is heated up to remove spores from cryptogams before combining it with the bio plastic. Woodcast which is a non-toxic alternative to commercially available casting and splinting material comes in two alternatives; the semi-rigid and the rigid model in thicknesses of 2 and 4 mm.

The material becomes pliable and self-adhesive when heated to 65°C and hardens as it cools down, similar to a thermoplastic. Icepacks can be used for rapid cooling of the cast [61].The heat insulating properties of woodchips in the cast prevents the skin from heat damage and the fabric like nature of the material provides the ability to cut with a pair of scissors without material tearing or wrinkling [74, 75].The material possesses 3D modality for better conformity.

Similar to plaster, this material can be handled without gloves and releases no aerosols during hardening [75,76]. According to Hirsimäki et al. [62], the material is self-adhesive and shows some adhesion to padding and other bandages as it possesses strong self-adhesive properties. Woodcast exhibit adhesion forces over 100N [61] making it difficult to be debonded without the use of a cast saw. Casts made out of Woodcast become load-bearing after 5-15 minutes of application with a stress yield of 15MPa and Young's modulus of 500MPa. Further, the material can withstand water exposure, possibly because the polymer matrix shields the woodchips from water absorption [58].

The design of Woodcast splints can be formed in such a manner that it can be removed during showering and reattached using brackets. Woodcast sheets contain parallel rows (17mm apart) of circular holes of diameter ≈ 9mm. Thus, allowing skin breathability. A study conducted on the biocompatibility and patient comfort of Woodcast on long term wear (6 weeks) using 33 patients with distal radius fractures showed that there were no allergic reactions and minimal skin abrasion [61].

According to Pirhonen et al. [63] the material shows equal stiffness to that of fiberglass tape. Studies conducted by researchers [58] and [64] showed Woodcast performs better than polyester and fiberglass under compression (at a width of 4mm when compared to 5-6 layers of Fiberglass tape), but performs two times lower than fiberglass in tension. Exposure to water, length of the curing and exposure to heat has no recorded negative effects on the material strength. Generally, cast material undergo more compressive loads than tension and the satisfactory strength characteristics of Woodcast makes it a safer alternative to synthetic casts.

Unlike plaster and fiberglass Woodcast has better radiolucency, enabling better x-ray diagnosis. The cast appears almost invisible in x-ray images generating clear images of the underlying trabecular bone [61]. The open design of the Woodcast enables the direct use of ultrasound imaging while in cast. Another major benefit of the Woodcast, is the ability to biodegrade after use either as bioenergy or compostable waste, causing no distress to the environment.

At present the design is limited to limb immobilization especially lower limbs and scaphoid casts. Existing studies have not directly proven the ability to treat wounds underneath the cast. Whereas, the ability to create open casts without full enclosure of the limb is possible. The ease in cast removal also provides some ability to treat those superficial wounds [55] [75,76].

2.4.1.2.6.2 Cellulose based casting material

A cellulose-compound cast was developed by Dr. PH Leavitt in 1933. The material immediately faced drawbacks of being extremely coarse and inflammable. Based on this development Thorndike and Garrey [65] constructed a cast material based on industry available cellulose product used to manufacture box toes for shoes.

Thorndike and Garrey [65] added Boric acid to cellulose to construct the light weight, hard and waterproof material. The cellulose compound was impregnated into fabric and applied as a cast after wetting it with a quick drying solvent. Although the developed cast is crude in nature and contains pyroxylin, boric acid and acetone, it can be applied similar to a plaster bandage. The cast is applied over a stockinet under adequate ventilation for drying.

The cellulose compound cast is far lighter than plaster, has extreme hardness, and is waterproof and translucent to x-rays. This cast can be worn in swimming and bathing activities due to its waterproof and lightweight. Compared to plaster only a small quantity of this material is required for adequate rigidity, but in comparison to synthetic material requires more drying time. It takes an average of 30-40 minutes to dispatch the patient but

cannot be indented until fully dried. Upon drying, the material has a higher inflammability index similar to that of dry wood [65]. The cellulose cast provides good workability and ease of application. However, it requires gloves to protect the appliers' hands from collodion-like films that flake off later on.

The cast has been tested for upper extremity fractures including Colles's fractures, fractured clavicles and double leg spica casts in children. Constructing jackets for arthritic spines and splints for deformity correction can be satisfactorily designed using this material.

During cast removal cutting and abrasion of the patient skin is a major risk. Hence, a felt strip (¼ inch) is included to provide protection during cast removal. Clinical trials have shown that the odour of acetone was unbearable when the cast was still wet but the odour subsided upon complete drying. No skin irritation was reported but flammability was recorded as a potential risk inherent to the material [65].

2.4.1.2.6.3 RECAST

According to [66] RECAST is a bio-based Polylactic Acid (PLA) plastic for fracture immobilization. RECAST splint material is developed by the Fraunhofer Institute for Applied Polymer Research (IAP), Germany.

A bio-based PLA plastic enhanced with necessary fillers is used in fabricating the splints with the ability to be easily reshaped and confirm to body contours.

The low thermal softening point of PLA allows the splint to be malleable when heated to 55-65°C. The material is reported to stay malleable from 30 seconds followed by 3 minutes post heating, before gradual hardening.

Similar, to most thermoplastic material this too can be reheated and reshaped. Further, the splint has fleece padding of PLA and Viscose for better patient comfort. As per manufacturer information, the splint can be applied only after swelling of the fracture site subsides which makes it inapplicable to fresh fracture sites and with swelling and inflammation.

The material is yet to be evaluated based on its mechanical properties, the load bearing capacity, patient comfort and biocompatibility. RECAST splints and liners are biodegradable using industrial composters [66]. Hence, this minimizes the environmental impact of hospital waste.

2.4.2 Cast padding and liners for skin shielding from direct cast contact

Simple cotton padding is the most commonly used cast liner. The affordability and higher degree of skin comfort have made cotton padding popular since the early 1852s [1]. Cotton padding readily absorbs water, perspiration and blood from the skin surface.

Cotton fibers upon absorption of blood, hardens constricting the immobilized limb [1]. Hence, incases of soft tissue swelling and edema, sterile cast padding that can stretch to accommodate swelling is recommended.

Today newer synthetic padding material is known to prevent skin irritation and are water resistant. Thus, allowing patients to bathe and swim. These are usually paired with synthetic casts such as fiberglass resulting in expensive casts that are low in affordability.

When used directly adjacent to the skin, closed cell foam padding is not recommended as it cannot effectively absorb moisture and urine from the skin. Hence, water permeable liners such as Gortex, are specially required in hip spica casts in pediatric and high-risk patient groups. Studies conducted by Stevenson et al. [67] show that waterproof cast padding is preferred by patients over cotton padding, especially the commercial brand Wet and Dry (3M) due to its odor and water resistance, while technicians prefer the commercial brand Delta Dry (BSN Medical) due to its ease in application and removal. It is still unclear whether waterproof padding or cotton padding is most suited in fracture alignment in unstable fractures although it shows no significance in stable fracture healing.

Studies have shown that thicker layers of padding act as an insulator entrapping body heat and increasing the temperature under the cast. Hence, the number of padding/webril layers and the cast thickness must be effectively managed to achieve higher patient comfort and reduce the risk of thermal injury [22]. Thicker layers of padding require plaster application under tension. This results in high friction between the cast and the skin, which can result in cast complications such as skin maceration. Hence, the proper application technique is desired for proper fracture healing and long term wearability of the cast.

Today, water proof cast liners are available in the market but some manufacturers still advise against the willful wetting of the cast.

2.4.3 Complications associated with Immobilization

Immobilization and cast removal are not without complications [1]. The major complications associated with casting are mainly investigated here.

Patients usually experience increased hair growth [7] [81] and decreased muscle bulk in the immobilized limb [68]. However, through proper techniques and attention to patient factors such as obesity, fracture location, age, skin condition and the intended activity level of the wearer, certain complications can be avoided. When applied over traumatic or surgical wounds extra attention should be provided to avoid the progression of complications. Proper assessment is mandatory in post-operative patients fitted to casts/splints [6]. Hence, all patient complaints regarding the cast must be examined by a medical practitioner and nurses have to closely monitor the patient condition after immobilization [69].

The major complications associated with cast immobilization discussed here, range from superficial nature to damaged underlying vasculature which requires surgical treatment.

2.4.3.1 Thermal burns

Lipid membranes of human tissues are highly sensitive to thermal energy [70]. Due to prolonged exposure to heat; proteins, enzymes, non-enzymatic metabolic pathways and physical alternations can occur in living tissues. Skin when exposed to elevated temperatures undergo transepidermal necrosis. Hence, prolonged exposure to heat has to be avoided during immobilization. Many commercially available cast materials undergo exothermic reactions when activated [27] [50] [83].

The risk of thermal injury is strongly associated with elevated temperatures underneath the cast. The contributing factors include high dip water temperature (>50°C) [71] [72], thicker casts (more than 24 layers) and lower ventilation during application. It is ideal to use no more than 12 layers of bandages and maintain dip water temperatures at 24°C [27] [82] [84] to reduce the risk of thermal injury. To avoid thicker casts, applicators have to be mindful of bandage overlap in concavities of extremities such as the antecubital fossa and ankle dorsum [22].

Halanski et al. [70] showed that placing a curing cast on a pillow and folding the edges of a splint can significantly increase the risk of thermal injury. Thermal injury is common from any cast material that reaches high elevated temperatures during curing and has longer curing periods [39], more significantly in thicker plaster casts with long curing periods due to prolonged exposure to elevated temperature [84,85]. Risk of thermal injury is higher in faster setting plaster casts than in slow setting thinner plaster [73]. Fiberglass tape is relatively safer than plaster, as fewer layers are required to achieve the required strength characteristics. Application of fiberglass reinforcement in hybrid casts, before complete curing of the plaster bandages can elevate the risk of thermal injury due to the inability of effective heat dissipation [50] [83].

In total body casts such as hip-spica casts adequate layers of padding and cast material has to be used to avoid thermal injury to patients. It is conventionally presumed that the increase of the layers of padding beneath the cast reduces the risk of thermal injury but studies have shown that thicker layers of padding entraps more heat. Using isopropyl

alcohol to reduce the temperature of a curing cast is effective on the outer surface but inner cast temperatures are minimally affected by this, with no significant reduction in thermal injury [70].

Use of ice packs between the limb and the pillow, holding the limb or allowing it to hang free can lower the risk of thermal injury during cast curing [70] [74].

2.4.3.2 Pressure sores

Areas of increased pressure leads to decreased perfusion which results in pressure sores. Children suffering from cerebral palsy related to surgery [75], casting for knee flexion contracture and hip instability have recorded higher probability of pressure sore development [1]. The signs and symptoms of pressure sore progression include pain and burning sensation, localized heat, cast odour, staining through the cast and pyrexia (in children) [69].

It may be rationalized that the use of extra layers of padding can relieve pressure sores but this results in a loose-fitting cast and risk of skin irritation due to high shear stress build up and fracture malalignment. Hence, application of adequate padding over bony prominences, pressure points and cast edges is recommended. Hence, the use of self-adhesive foam padding such as Reston self-adhering foam (3M) over pressure sensitive areas is recommended.

A well-trained technician or physician should carry out cast application to prevent pressure sore development, as this is generally associated with poor casting techniques. The cast should be a well moulded fitting cast to minimize excessive pressure buildup.

Wrinkling of the cast material and movement before complete curing creates edgy prominences which can result in pressure sores. This is commonly seen in synthetic casts with low curing times [69].

The detection and prevention of pressure sores can be achieved through properly placed cast windows in high risk patient groups and to examine open wounds [13]. Cast windows are prominently required to release pressure when Kirschner wires and external fixation devices are included in limb immobilization. Univalving and bivalving are also commonly used to release pressure entrapped underneath the cast [39].

2.4.3.3 Skin irritation and maceration

Patients often suffer from itching due to wetting of the casts or sweating, which results in foul odor and skin irritation [68]. This is critical in hip-spica casts where cast soiling is a major issue due to water and excretion coming into contact. Thus, it requires waterproofing.

Blisters, erythema, contact dermatitis are common among 13% of the cast wearers. Clinical studies record dermatitis associated with plaster casts is due to Benzalkonium Chloride used to improve plaster binding characteristics and melamine formaldehyde resin used in plaster resin casts [76].

Traditionally, casts are lined with a stockinet and cotton or synthetic padding. Cotton padding when exposed to blood and water retains moisture causing skin irritation and maceration [1]. Loosely fitted casts result in higher degrees of skin irritation and abrasion due to shear stress build up in the skin-padding interface. In case of cast wetting patients

and their caretakers are instructed to dry the outer cast with a towel and use a blow dryer on a low temperature setting when drying the inside of the cast [77]. This extracts the moisture that otherwise can cause skin maceration and irritation. Patients are warned against using sharp objects to scratch beneath the cast as this can risk infection and skin abrasion.

Temporary treatments for cast related skin irritation include antihistamine medication, blowing cool air down the cast and applying calamine lotion [78] before cast application. New synthetic material and waterproof liners have shown improvements in preventing skin irritation, cast odour, patient satisfaction and allowing patients to swim and bathe. Studies show that covering the cast with a plastic bag while bathing is most effective against cast wetting [79]. Although improvements are underway, the optimal cast liner and material to reduce itching and skin maceration are yet to be determined.

2.4.3.4 Compartment syndrome

Inflammation / swelling of the fracture site and soft tissues may or may not be present during cast application. Increased tissue pressure within a limited space, compromising circulation and tissue function can lead to compartment syndrome. Compressed neurovasculature limits blood flow damaging muscles and nerves which can lead to extreme pain. Patients with nerve damage may not experience pain due to compartment syndrome, but may exhibit sensory and ischemia related symptoms. After the onset of nerve related ischemia full recovery is impossible.

Compartment syndrome can lead to major complications such as limb amputations and even mortality. Hence, special attention has to be paid when applying casts of low elastic modulus like fiberglass and tacky PU resin bandages, to avoid limb constriction and avoid areas of high-pressure buildup [80].

Compartment syndrome is an anticipated complication in hip spica casts. Hence, it is recommended to apply traction or stretch-relax [80] the cast material using hand and end the cast in the supramalleolar region with the hip and knee flexed at 45° [81]. Many studies show that stretch relaxing synthetic tape and relieving circumferential pressure via cast splitting is effective to reduce compartment syndrome [1] [21] [92] .

Clinical studies have shown that plaster cast cutting and univalvling reduces pressure by 40-60%. A further 10-20% pressure reduction can be achieved by splitting the underlying layer of padding. Zaino et al. [82] show that casts made of fiberglass applied without stretch-relaxation is two times tighter than plaster casts. Hence, bivalving is required for a similar reduction in pressure entrapment. For stretch-relaxed fiberglass casts univalving is adequate to spread and keep the cast in open. As synthetic casts have the tendency to spring back to their original position after univalving, plastic cast wedges are required to hold them in an open position [47].

After pressure relieving, it is recommended to elevate the extremity no higher than the heart to maintain arterial perfusion. In extreme situations fasciotomy is required to relieve pressure to prevent the progression of tissue necrosis and nerve ischemia [3] [69].

2.4.3.5 Deep Vein Thrombosis (DVT)

Deep Vein Thrombosis (DVT) is significantly seen in the adult population with prolonged lower extremity immobilization [1] [14]. Studies have shown that the probability of DVT is 15 to 36% in adults, when placed in lower extremity casts for an average of 21 days.

Low molecular weight heparin use does not show any significant reduction in DVT even when administered daily [1]. Secondary complications such as pulmonary emboli or death have not been recorded due to cast induced DVT. It is recommended to use less rigid methods of immobilization such as splints and softer casting material such as Softcast (3M) to reduce the risk of DVT.

2.4.3.6 Soft tissue swelling

Soft tissue swelling is common in the fracture site and generally subsides after 48 hours. Long term prevalence of such post traumatic edema can result in excessive cast tightening and soft tissue injury, which can lead to secondary complications such as muscle atrophy, compartment syndrome, Volkmann contracture and transdermal necrosis. Fast setting casts such as PU resin and Fiberglass accommodates less soft tissue swelling than plaster casts that has a longer curing time.

Zaino et al. [82] with a stimulated edema-induced pressure setup for a short arm fiberglass cast concluded that single cut (bivalving and ace wrapping) method could reduce skin surface pressure caused by edema by 70.8%, while the most effective is the triple cut method (bivalving, spreading, webril cut and ace wrapping) which recorded a 99.9% reduction in edema induced pressure in fiberglass casts. The study suggested that women

register higher skin surface pressure (104.4 mmHg) than men (81.1 mmHg). Hence, women are at a higher risk of succumbing to edema induced pressure complications when placed in casts [82].

Contrastingly, the gradual decrease in edema results in cast loosening which can cause significant displacement of the well aligned fracture which may require cast replacement or reapplication. This is a common complication in unstable fractures especially in lower extremities. Studies have shown that cotton padding best behaves in pressure release in splitting and accommodation of swelling than synthetic padding [83]. Cotton padding has its drawbacks when exposed to blood. The cotton fibers harden and can be constrictive of the encased limb resulting in edema [1].

Proper elevation to subside swelling and the use of adequate padding can reduce the risk of complications associated with cast loosening or development of high pressure areas. In cases of significant soft tissue swelling associated with unstable fractures percutaneous pin fixation is recommended primarily. However, percutaneous pin fixation has its own merits and drawbacks [84] .

2.4.3.7 Venous congestion and hematoma

Impaired venous return due to tight casts can cause swelling or bluish discoloration of the immobilized limb. This venous congestion induced bluish skin discoloration has to be properly identified apart from bruising in patients to avoid poor perfusion [1] [14]. Tight fitted rigid casts can lead to the development of venous congestion. Thus, in patients with a risk or a history of venous congestion, rigid immobilization has to be carried out by

licensed practitioners. Orthopedic practitioners recommend the use of splints and cast univalving to lower the risk of venous congestion.

Hematoma or bleeding under the cast is seen especially in post-operative patients with trauma wounds. The brownish staining of the plaster casts can be observed in cases of hematoma. Studies have shown that significant brownish staining depicting blood underneath the plaster cast can only be seen after 24 hours of immobilization and complete drying of plaster casts. The staining of the cast depends on the cast and padding thickness, post-operative patient positioning, the extent of trauma and the hemostasis technique. Mild hematoma can easily go unnoticed. Therefore, extra caution is required when fitting post-operative patients to casts. Existing literature shows a lack in the identification of hematoma in relation to synthetic casts [6].

2.4.3.8 Cast saw burns

Rigid casts specially fiberglass and PU resin casts require cast saws for removal. Studies report a 0.72%-1% frequency of cast saw burns during cast removal, which are thermal or abrasive in nature [1] [82]. Technicians have to take precautions to avoid cast removal complications especially when using cast saws for removal of casts with waterproofing liners.

Keeping the patient steady and calm is required to prevent vibration related injuries especially in pediatric groups. Puddy et al. [85] have shown that bulkier casts require higher oscillation speeds resulting in high blade temperatures. Technicians have to be careful not to overheat the saw blades when cutting long casts and allow the blades to cool

during the procedure to avoid burns and cuts. Proper inspection of the blades, frequent blade changes, use of sharp blades, avoiding sliding of the oscillating saw along the cast and using proper cutting techniques can greatly reduce the risk.

Studies [97, 98] show that cast saw blades can reach dangerously high temperatures like 70°C or 123-130°C during operation that can even result in second- or third-degree burns. It takes a minimum of 2 minutes for the blades to cool down to safer operating temperatures. Application of 70% isopropyl alcohol, ultrasound gel and water to the heated blades can speed up the cooling process. According to Puddy et al. [85] the most effective cooling technique is the application of 70% isopropyl alcohol to the padding/ dressing.

Cutting along safety strips which are less heat resistant than the cotton padding results in low heat generation during removal. Use of plaster shears , built in metal / plastic strips and easy wrap cast- made of thermosetting polymer that is mounted between the two edges of the cast material are other alternatives to cast saws [3] [86] are recommended. Cutting underlying padding using trauma shears ensures no damage to the patient's skin [3], whereas in Thermoplastic cast removal can be done by heating and cutting with scissors. In clubfoot plaster casts, cast wetting is recommended for removal.

2.4.3.9 Cast dust and cast ingredient associated complications

Long term exposure to dust particles and ingredients such as isocyanates that arise from crude cast material can result in occupation related asthma and other breathing disorders. This is mainly seen in fiberglass and PU resin casts. There is a very low probability of

asthmatic reactions related to Methylene Diphenyl Diisocyanate (MDI) in casting of plaster casts. Hence, it is precautionary to avoid exposure to even very low concentrations of MDI [87].Similar consequences are reported due to exposure to cast dust that arise during cast removal. To minimize occupational asthma and ensure user safety, modern cast saws are equipped with a vacuum extraction accessory [2].

Studies have reported carcinogenic risks associated with the manufacturing of synthetic casts such as PU resin bandages and Fiberglass tape [1]. Cases of acetone poisoning have [88] been reported in synthetic casts. Acetone is used as a solvent evaporator in synthetic casts. There are no records of acetone absorption through the skin hence inspiration of acetone by the lungs can result in acute acetone poisoning. This can even result in comatose if inhaled in large quantities over a prolonged time. Thus, synthetic casts are eliminating the use of aerosol and breathable toxic agents.

2.5 Discussion

Based on the findings of the systematic literature review and the comprehensive analysis provided under Section 4, the following details can be extracted. A comprehensive summary is given under Appendix 1

Appendix 1 shows each immobilization material against the risk of common complications they are likely to be associated with.

Hence, it can be seen that plaster shows moderate probability of causing common complications while synthetic and other material are highly likely to cause serious

complications. Further, plaster is still the material of choice in full body casting while newer material is more used for short term extremity casting and splinting.

2.6 Challenges and opportunities

Based on the findings and the discussion it is identified that the most common challenges in immobilization are;

1. Ability to accommodate swelling and treating the wounds under the cast is a huge challenge which can lead to complications when fitted to casts. This is a requirement in diabetic foot care and accident trauma management.
2. Proper disposal of synthetic casts and upcycling of synthetic cast material is challenging due to their toxic ingredients and nonbiodegradable nature.
3. Waterproofing of casts and cast permeability to moisture on skin opposes each other. Both factors are sought after in terms of patient comfort.
4. The low conformity of synthetic casts causes pressure entrapment in extremity casting.
5. Majority of immobilization material have tacky ingredients that makes it messy in application and removal.
6. Toxic ingredients in casts and dust cause asthma and other respiratory distress to users.
7. Plaster has undergone minimal alterations to its performance despite its high use especially in full body casting.

8. Monitoring the progress of fracture healing and wound healing is difficult without cast removal due to low radiolucency of casts.

Despite these challenges the following opportunities are identified by the authors:

1. Development of material with low risk of complications, higher patient comfort and eco-friendliness with adequate mechanical performance.
2. Improving the strength characteristics and waterproofing ability of plaster especially for full body casts
3. Development of a cast lining or casting material that can accommodate swelling and hematoma under the cast for trauma patients and post-operative patients.
4. Using sustainable fillers to improve strength and comfort of immobilization material.
5. Upcycling and circular economy for synthetic and other immobilization material.
6. Development of waterproof liners and highly breathable casts for full body and long body casts.
7. Improving the radiolucency of casts and splints to avoid cast removal in patient monitoring.

Paper 02

2.7 Investigation of sustainable filler material for modification of plaster

Cohen and Frillman [89] has shown that organic material is a safer alternative to synthetic fiberglass casting as synthetic material are not ecofriendly and register minimal thermal comfort and conformity to body contours. Hence in improving traditional plaster the use

of organic material is an ecofriendly and sustainable option. Agricultural waste and naturally occurring biomimetic surfaces can be used to improve the thermal comfort, breathability and resistance to water degradation of plaster casts.

2.7.1 Rice Husk Ash

Rice husk is an agricultural waste material generated by rice milling countries like Sri Lanka, China, Myanmar and India, where paddy-based agriculture is abundant. Rice is one of the abundantly cultivated agricultural commodities in Sri Lanka, with a per capita consumption of 191 kg in 2021. This leads to a huge quantity of Rice Husk production following rice processing, which eventually ends in open fields and landfills. Today with sustainability being a prominent concern, rice husk is incorporated into polymer composites and as an additive in cement and concrete, gaining the attention of many researchers.

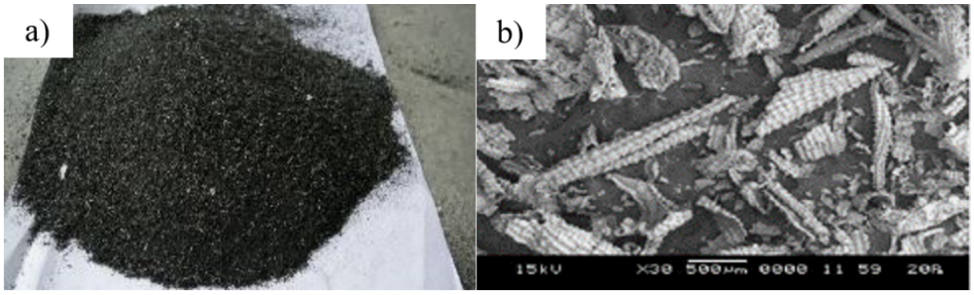

Figure 6: a) Open burnt RHA b) RHA microstructure under SEM

Rice husk is abundantly used as Biomass in generation of electricity which is roughly 25% of the disposed Rice husks. Rice husk when burnt at very high temperatures (700-800°C) generates RHA [90]. Although highly reactive RHA can be obtained under controlled combustion, which is not an economical option for bulk production. Hence industry grade applications use RHA produced under uncontrolled combustion [91, 92]. However,

burning alters the chemical composition of RHA based on the burning process and temperature. At higher burning temperatures the Silica content of RHA increases.

The physical properties of RHA are tabulated below;

Table 2: Properties of RHA

Description	Physical property
Colour	Gray
Texture/ shape	Irregular
Mineralogy	Non-Crystalline
Particle size	>45 Microns (uncontrolled burnt)
Odor	Odorless
Specific Gravity	2.3

2.7.1.1 Composition and properties of Rice husk Ash

According to Sevarajan et al., RHA comprises of 38% cellulose and 20% ash, 95% of the ash is SiO_2 [90]. Refer Table 3.

Table 3: Composition of RHA

Composition	Weight %
Silicon dioxide	86.94%
Aluminum oxide	0.2%
Iron oxide	0.1%
Calcium Oxide	03.-2.2%

Magnesium Oxide	0.2- 0.6%
Sodium Oxide	0.1-0.8%
Potassium Oxide	2.15-2.30%
Ignition Loss	3.15-4.4%

2.7.1.2 Pozzolanic Activity of rice Husk ash

ASTM C618 classifies finely ground RHA as an F type pozzolan material as the summation of SiO_2, Al_2O_3 and Fe_2O_3 is more than 70-80%. This pozzolanic property of RHA makes it a substitute for gypsum replacement in cement and concrete. Morsy and Mohommed [93] show that RHA needs a slightly alkaline environment for pozzolan reaction but gypsum provides a slightly acidic or neutral environment, hence some alkalinity is essential for proper binding activity.

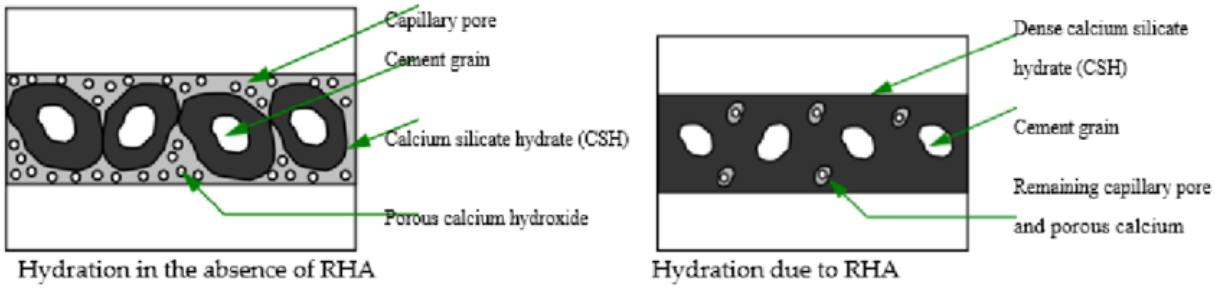

Figure 7: Pozzolanic activity in the presence of RHA particles in concrete

2.7.1.3 Behavior of RHA in plaster composites

RHA-gypsum composites show notable improvements. Use of agricultural by products and natural fibers, have shown significant improvement in thermal conductivity of composites Studies have shown that RHA possesses good mechanical strength and is a

good absorbent which can effectively improve the porosity in mixtures. Studies investigating the thermal properties of Plaster of Paris –RHA composites for thermal insulation applications show that 40% RHA as a filler by composition in POP celling boards recorded thermal conductivity as low as 0.111 $wm^{-1}K^{-1}$, proving good thermal insulating characteristics of RHA [94]. Studies conducted by Amulah et al. [95], recorded 0.231 $W \cdot m^{-1} \cdot K^{-1}$ and 22.114 m^{-1} in thermal conductivity and specific heat capacity of samples containing RHA, bagasse and saw dust. Further, increase in RHA composition in mixtures is known to increase the specific heat capacity of the resulting composite, proving that RHA increases the capacity to absorb heat providing thermal comfort. Using RHA as a filler in composites reduces the density of the resulting mixture making composites lighter and with good porosity [96]. Studies conducted by Amulah et al., evaluates the thermal properties of RHA -gypsum plaster composites as a potential insulating material, which records significant reduction of thermal conductivity, improving its insulation capacity of 40.3% in 40% RHA additions [95].

Studies conducted by Selvaranjan et al. [90] showed that when studying the microstructure of mortars comprised of RHA, the increase of RHA in the ad mixtures improved porosity. This is due to the increased number of pores created by evaporating water that were absorbed by RHA particles. According to this study, the pores formed by evaporating water get filled with air reducing the thermal conductivity. They have found that for 24.17% and 30% RHA replacement of sand thermal conductivity was significantly reduced due to increased porosity. Finer RHA with a high amorphous Silica content improves the compressive strength of cementitious mixtures Chauhan et al. [94] show that

Silica extracted from RHA reduces the crack build up in Plaster of Paris- RHA (Silica) composites even under high temperature conditions. Selvaranjan et al. shows that 30% RHA replaced sand in mortar plaster can reduce 10% heat flux and 9% energy requirement reduction for thermal comfort maintenance, while maintaining adequate compressive strength. Incorporation of additives such as RHA into gypsum alters its water absorption and mechanical properties.

Therefore, RHA incorporated into POP can be a viable option to improve the breathability of the casts due to improved porosity, reduced thermal conductivity, improve mechanical strength of plaster casts and reduce the weight of the resultant cast. Rice husk is an abundantly found, low cost, low density and no hazardous agricultural waste product. So, is open burnt rice husk ash, which serves as low density, nonabrasive, biodegradable and low energy consuming filler material in composite development. Studies refer to RHA used as a filler in gypsum plaster where mechanical properties and thermal properties of plaster composites and to reduce the weight of the resultant cast.

2.7.2 Graphene Oxide

In the last decade of nanomaterial technology and research scholars have carried out extensive investigations into Graphene. Graphene received strong research momentum and widespread attention due to its remarkable properties and applications. Graphene is a 2D nanosheet which translates to the two-dimensional form of graphite. Among graphene nanomaterial-based research graphene nanoplatelets, graphene oxide (GO) and reduced graphene oxide (rGO) are the most popular. GO consist of several layers of wrinkled two-dimensional carbon sheets with various oxygen-containing functional groups such as

hydroxyl, carboxyl, and epoxy on its surface or between the inter-sheet layers. Most of the existing research on the use of graphene is based on GO [97].

Sri Lanka is the only country in the world, in which vein graphite is available. Vein graphite is extremely high grade (high purity) with over 90% carbon. Graphite oxide is made by oxidation of natural graphite. Sonication in a chemical mix produces GO.

GO acts as a catalyst improving the hydration of mixtures, especially in cementitious

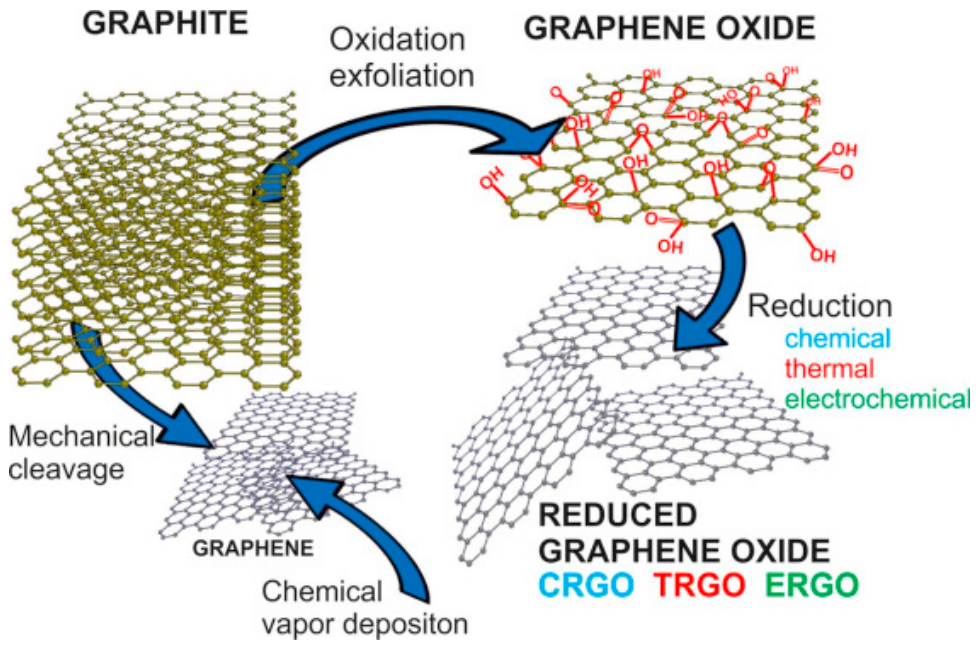

Figure 8: Conversion of graphite to graphene oxide and to reduced graphene oxide and into graphene *[132]*

composites. GO sheets act as nucleation sites for the hydration products. Thus, improving the mechanical strength and reducing the setting times. GO possesses an average fracture strength and elastic modulus of 80 MPa and 32 GPa, respectively. According to Kim et al. hydrated GO films are permeable to water molecules to a higher but dry GO films are highly impermeable to small gas molecules, such as hydrogen and helium. The gas barrier for entering the GO sheet is reliant on residual water content, thickness, sheet size,

structure, and structural distortion created through the dewetting processes [98]. The sp2 -hybridization of strong C=C bonds in GO leads to efficient heat transfer via vibrations in the lattice and phonon transport models. The oxygen functionalities in GO allows it to be readily be dispersed in water, in diverse solid matrices, and in organic solvents. Thus, allowing the formation of composites with may enhanced thermal and mechanical properties. Further, literature shows that minute quantities of GO such as 0.02% to 1% by weight of the residual mixture is required for strength and performance improvement [99].

2.8 Chapter Summary

This chapter discusses the development of immobilization materials, their properties, and their effect on patient comfort and satisfaction. The following conclusions can be made:

1. The history of immobilization materials extends to 3000 BC, which initiated with splints designed from sticks and palm fiber bandages, gradually transitioning to plaster in 1798. Developments in casting have taken place considering patient satisfaction, mobility and better mechanical properties.
2. Even though there are new materials such as polyurethane impregnated fiberglass, polyurethane resin, thermoplastics and silicone rubber are available, still the most favorable and cost-effective solution for immobilization in many countries is plaster.
3. An immobilization material should possess required material properties such as adequate mechanical strength with tensile strength > 20 MPa, flexural modulus >2 kN/mm^2 and failure loads >10kN with the ability to bear cyclic loads, faster setting

times, waterproofing ability and quick drying time, faster and less messy application, composition of non-toxic, non-flammable and non-irritant constituents that can be activated using low heat or undergo mild to moderate exothermic reactions when immersed in water, good cast breathability and vapor permeability, ability to accommodate swelling and edema, ability to be used in long term immobilization (exceeding 4 weeks), excellent conformity with no pressure point generation, good radiographical properties and economic feasibility, for higher patient comfort and an efficient healing process. Out of the available materials the synthetic materials only satisfy the strength requirements.

4. The patient comfort is a compulsory matter in the process of long-term immobilization. In this regard breathability, thermal comfort, water resistance, lightweight and non –toxicity (non-irritant) are important. Only Woodcast material possess a majority of these characteristics.
5. The most common complications in fracture immobilization are skin irritation and maceration, pressure sores, thermal burns, soft tissue swelling and cast saw burns. These complications mainly occur due to early stage heat generation, low porosity, and low conformity to body contours of immobilization materials. Hence, it is important to consider these properties as the top most priority, in the process of developing an immobilization material.
6. Setting time is another key factor considered in the development of immobilization material. If a cast possesses a low setting time the patient can be discharged to his familiar environment which ensures the psychological well-being of the patient

and is also beneficial to maximize routine activities. This can be achieved through the addition of accelerators in the development process of the cast material.

7. In comparison of the available cast material under low cost, patient comfort, lower cast complications and setting time, the following order of choice can be achieved arranged in ascending order:
    - Cost: plaster of paris< silicone rubber < fiberglass- plaster hybrid < thermoplastic < fiberglass < PU resin < Woodcast
    - Patient comfort: Silicone rubber< thermoplastics< plaster of paris< PU resin< fiberglass< Woodcast
    - Lower cast complications: synthetic casts < plaster of Paris
    - Setting time: RECAST< thermoplastics< PU resin≤ Fiberglass < Woodcast<plaster+ fiberglass hybrid< plaster of paris < cellulose based material< Silicone rubber

    (Properties can vary according to the brand and additives used.) (Refer Table 2)
8. Further modifications to the existing orthopedic immobilization materials are required for superior strength gain, improved material characteristics, lightweight and superior patient comfort. Therefore, it is required to modify the abundantly used plaster cast material to gain the aforementioned properties. Graphene Oxide is considered in the work carried out in the University of Moratuwa to achieve this objective.

9. RHA is a good thermal insulator which can prevent the heat emanated from plaster setting to cause thermal burns on adjacent skin. Thus, improving early thermal comfort.
10. RHA also reduces the density of the final product, resulting in a light weight composite.
11. GO is known to act as a catalyst, improving nucleation and reducing cast setting time. The exemplary mechanical properties of GO have the potential to improve the mechanical strength of traditional plaster.
12. GO reduces the water permeability when wetted and maintains good dispersion in mixtures. Thus, reduces the water degradation of the overall composite.

CHAPTER 3- MIX DESIGN OPTIMIZATION

3.1 Introduction

This chapter provides a detailed overview of the preliminary studies carried out, which enabled the development/ replication and optimization of the control mix and afterwards the sustainable filler incorporated mix designs. According to the observations and results gathered through the preliminary study, the shortcomings and material selection for the final design was clearly identified.

3.2 Phase I- Control sample development

3.2.1 Material selection and sample preparation

The actual recipe of commercially available orthopedic plaster is a trade secret. However, through thorough investigation into existing literature and patents, the material selection for the control mix was derived from Lewry, A.J [100]. The original mix design derived from the [100] is tabulated below:

Table 4: Original mix design developed by Lewry *[100]*

Material		Composition wt%	Composition (g)
$CaSO_4$ hemihydrate	α	95	285
	β		570
$CaSO_4$ soluble anhydrite			95

$CaSO_4$ dihydrate	2	20
K_2SO_4	1	10
PVA	1	10
Hydroxy propyl cellulose (HPMC)	1	10
Total	**100**	**1000**
800mL of Dichloromethylene (DCM) for 1kg of total mix		

3.2.1.1 Selection of $CaSO_4$ hemihydrates

In the selection of α and β $CaSO_4$, commercially available medical grade plaster used in the making dental molds were used. It was identified that Type 5 dental plaster is α $CaSO_4$, while type 2 dental plaster is β-$CaSO_4$ [101]. α-$CaSO_4$ is more crystalline than the β form and forms a stronger set plaster. However, initial setting time is much higher in comparison to β- $CaSO_4$. α-$CaSO_4$ forms multiple small crystals which are short and sturdy. Hence, lower strength than the α variety. This however sets much faster than α-$CaSO_4$, giving faster setting times. Considering all these factors previous studies recommend using a mix of α: β as 1:2 [100].

Literature states that γ. $CaSO_4$ and $CaSO_4$. $2H_2O$ does not have a profound effect on the strength gain of the plaster. Hence, this was eliminated from the mix design developed for this study.

3.2.1.2 Selection of Binders

PVA glue and hydroxypropyl methyl cellulose (HPMC) were used as binders to adhere the plaster to the underlying bandage. These binders were only used in developing plaster bandages but was eliminated in casting cubes for compression testing under Chapter 3 and 4. However, their effect on plaster was critical to understand the behavior of the microstructure and were added to the blends tested in Chapter 5. PVA was obtained from a commercial supplier for the sample development along with hydroxypropyl cellulose and Dichloromethane (DCM). Under phase I, PVA crystals were used in sample preparation as DCM dissolves PVA.

In the latter stages of the preliminary study PVA crystals were switch to commercially obtained PVA glue. Most commercial suppliers add formaldehyde as a preservative to PVA glue for longer shelf life. This can react with some of the additives when in a solution. Hence, the constituents and water content of the PVA glue has to be taken to account. The composition breakdown of commercial PVA glue used for this study is as follows;

- 20% PVA in 100g of total glue solution (2g PVA in ≈ 7.9mL of H_2O)
- Preservatives used: Formaldehyde 1%

3.2.1.3 Selection of accelerators and nucleating agents

K_2SO_4 was used as a nucleating agent and accelerator. The composition selected was based on existing literature [100], as compositions above 2% has shown detrimental

effects on the ultimate strength gain of the plaster. K_2SO_4 was maintained at 2% for all mix designs developed.

3.2.1.4 Selection of solvent

The solvent was selected based on its ability dissolve materials to form a homogenous slurry. Luke warm water was the ideal candidate for mixing, as PVA and $CaSO_4$ both dissolves well in water. However, hemihydrate $CaSO_4$ undergoes exothermic conversion to dihydrate $CaSO_4$ cutting down the preparation time. Thus, it was difficult to prepare the initial mix without hardening of plaster in the mixing bowl. Studies [102] have used DCM as a solvent for preparation of plaster, as DCM allows preparation time of ≈ 15 mins. Further, DCM is volatile and evaporates from the final mix without changing the composition.

3.2.2 Method of preparation

41 As stated in literature, a similar methodology was mimicked in the control sample development. Existing literature uses a mixing tank with four baffles fitted to prevent the formation of a vortex during the stirring process [100]. However, in this study a scaled down version was implemented with a mechanical stirrer (Refer Figure 9).

Figure 9: Mechanical mixing of the control mix using a hand-held mechanical stirrer.

Table 5 provides the weighted compositions of raw materials used in the control blend preparation.

Table 5: Mix design for control blend

Specimen Category	Composition by weight					DCM (mL)
	Plaster (α:β =1:2)		K_2SO_4 (g)	Binders		
	α (g)	β (g)		PVA (g)	HPMC (g)	
Control	96	192	6	3	3	240

Composition for 300g of control blend

Pre-weighted amounts of the binder were added to Methylene chloride / DCM added to the mixing jar. Mixing was carried out until the binders were completely mixed and a foamy slurry was obtained (Mixing time= 2 minutes). Next, the rest of the formulation was added to the mixing jar and mixed for another 3 minutes until a homogenous mixture was obtained. Finally, the slurry was transferred to pre-weighted cotton bandages of 1m in length and spread evenly using a palette knife.

Commercial cotton bandages available had a lower thread count, hence it was made 2 ply to obtain the desired thread count of 46 threads per square inch. This supports better adhesion of the plaster slurry to the bandages and reduces flaking off and material loss when drying.

3.2.3 Problems encountered in Phase I

3.2.3.1 Dichloromethane (DCM) toxicity

The binders, especially PVA is soluble in both polar solvents such as water and DCM. Plaster of paris doesn't undergo exothermic conversion to gypsum or Calcium Sulfate Dihydrate when mixed using DCM. Plaster and DCM undergo an endothermic reaction, thus making it easier to form a spreadable slurry with adequate time to transfer into molds or bandage. Based on this, studies have replaced DCM as the solvent instead of water.

However, DCM is carcinogenic and can damage the skin, lungs and liver when inhaled or upon skin contact and is considered a hazardous solvent. Thus, the material was discontinued from regular use by the FDA and requires a fume hood and adequate ventilation if used [103].

In this study the use of DCM within the existing laboratory conditions was hazardous and caused breathing difficulties, nausea and drowsiness. Thus, a replacement was required to carry out sample preparation.

3.2.3.2 PVA agglomeration

PVA crystals were added to DCM and mechanically stirred to form the binder paste. Due to the inconsistency of mixing and high volatility of DCM, the PVA crystals did not properly dissolve to form a homogenous paste. Even within the plaster-binder slurry agglomerations of PVA was found along with undissolved PVA crystals.

3.3 Altering the pathway -Phase II

3.3.1 Replacement of PVA crystals with PVA glue

Owing to the issues faced with PVA agglomeration and partial dissolution. PVA crystals were replaced by PVA glue (Refer 3.2.1.2) form a commercial supplier.

3.3.2 Replacement of DCM with water and an inhibitor

Although rapid setting of plaster is required in the application phase, in preparation of the initial plaster adequate time is required to mix the material together and spread it on to the bandages or the molds. Luke warm water which is a polar solvent is excellent in dissolving PVA and HPMC but reduced workability due to $CaSO_4$ undergoing rapid exothermic hardening upon exposure to water.

This demanded the use of an inhibitor to retard the action of $CaSO_4$ and water while providing adequate time for sample preparation. However, the retarder should not increase the setting time which is a drawback in plaster application, limiting the dispatch and mobility of patients.

According to [104], an Ammonium Borate was used an inhibitor along with water. The Ammonium Borate inhibitor, slows down the setting process of plaster while dissolving PVA. In order to form Ammonium Borate (NH_4BO_3), Ammonia [NH_3(l)] and Boric acid [H_3BO_3] were mixed together, in the quantities tabulated below;

Table 6: Preparation of the control blend with Ammonium Borate

Type of $CaSO_4$	Quantity of material used			
	$CaSO_4$ (g)	H_2O (mL)	H_3BO_3 (g)	NH_3 (mL)
α hemihydrate of CaSO4	100	70	0.35	0.175
β hemihydrate of CaSO4	100	70	0.65	0.33

Considering the above quantities, the following mix design was developed:

Table 7: Mix design with NH_3 Borate retarder

Specimen Type	Composition by weight									
	Plaster (α: β =1:2)		K_2SO_4 (g)	Binders		Retarders		Additive		Water (mL)
	α (g)	B (g)		PVA (mL) (20% PVA)	HPMC (g)	NH_3 (mL)	H3BO3 (g)	RHA (g)	GO (mL) 10g/L	
Control	85.5	171	6	30	3	1.2	2.4	0	0	216
Plaster +RHA	85.5	171	6	30	3	1.2	2.4	15	0	216
Plaster + GO	85.5	171	6	30	3	1.2	2.4	0	15	201
Plaster+GO+RHA	85.5	171	6	30	3	1.2	2.4	15	15	201
				PVA 40-40:160		Mix NH3 and H3BO3 in 20mL of water			0.05g of GO	

Mix Design Optimization

				(PVA:water) 20% PVA					

In the preparation of the samples using NH_4BO_3 inhibitor, the following steps were followed;

Step 1: weigh the required quantities according to Table 7

Step 2: Add Boric acid to half of the batch water

Step 3: Stir until the acid is thoroughly wetted

Step 4: Add NH_3 to the mix and continue stirring until a clear solution results

Step 5: Add the binder paste (PVA glue and HPMC)

Step 6: Add the accelerators or fillers (K_2SO_4)

Step 7: Add the weighed plaster to the resulting mixture

Step 8: Mix using a mechanical mixture until a homogenous slurry is formed

(Mixing time – 5 to 8 mins for quantities provided above)

Step 9: Transfer the slurry to molds or bandages and coat

Total mixing time should not exceed 15 mins.

NH_4BO_3 inhibitor provides a total inhibition time of approximately 20 minutes.

Although, NH_4BO_3 retards the setting time of plaster during manufacturing providing adequate time (20 mins- based on the quantities provided under Table 7) for bandage/sample preparation. During the application process this retardation is a drawback which slows down the hardening of the final cast.

Hence, after preparation of the plaster it is important to decompose the inhibitor to avoid setting time retardation of the final cast. Accordingly, the prepared bandages were heated at 154^0C for 3 mins or at 85^0C for 15 mins, to break down NH_4BO_3.

$$4NH_4BO_3 = NH_4HB_4O_7 + 3NH_3 + H_2O$$

$$4(NH_4)_3BO_3 = NH_4HB_4O_7 + 11NH_3 + 5H_2O$$

$$4(NH_4)_3BO_3 = NH_4HB_4O_7 + 7NH_3 + 5H_2O$$

$$NH_4HB_4O_7 + 5H_2O = 4H_3BO_3 + NH_3$$

Hence, the mix design was altered as tabulated below (Refer Table 8) to incorporate Ammonium Borate and water for preparation. The mix design incorporates the H_3BO_3: NH_3 in the ratio of 1:0.5112 or 1.956:1.

Figure 10: Ammonium Borate retarder mixed with a portion of batch water.

3.3.3 Precautions to follow when using NH_3

NH_3(aq) like DCM is volatile and forms NH_3(g) which has a pungent odor and can cause difficulty in breathing and irritation of skin and eyes. Too much NH_3(g) inhalation can lead to NH_3 toxicity that can negatively affect the health of the user. Thus, wearing safety gloves, goggles and using NH_3(aq) in a well-ventilated area should be followed.

In case of NH_3 contamination with skin or eyes, wash them immediately with water.

3.3.4 Issues encountered

The commercially obtained PVA glue contained formaldehyde as a preservative. Formaldehyde and NH_3 from the inhibitor reacts, solidifying PVA glue, forming hexamethylenetetramine.

$$6HCHO + 4NH_3 = (CH_2)_6N_4 + 6H_2O$$

Thus, the commercial supplier was requested to remove any additive and preservatives from the glue solution and the water- PVA (20% PVA) solution was used in the sample preparation.

3.4 Modification of the control plaster – Phase III

In order to provide higher thermal comfort and better patient comfort when placed in a plaster of paris cast, this study incorporates Rice Husk Ash (RHA) as a sustainable filler. Also, Graphene Oxide (GO) was used as a filler to provide higher strength. Literature

states that RHA reduces strength and GO can effectively regain strength acting as a catalyst in hydration and can improve water resistance to the resulting mix.

The following table elaborates the mix design for RHA and GO addition. Here, plaster composition was not replaced by RHA or GO. The initial design compositions were kept constant while 5% of RHA and 5% of GO (10g/L) were added as shown below.

(*Note: the amount required for two samples of each category are provided here, refer Table 8 for required percentages*)

Table 8: Mix design with retarder and Graphene Oxide

Specimen category	α- $CaSO_4$ (g)	β- $CaSO_4$ (g)	K_2SO_4 (g)	RHA (g)	GO (10g/L)	H_3BO_3 (g)	NH_3 (g)	H_2O (mL)
Control (C)	106	213	6	-	-	2	0.8	180
RHA-Plaster	106	213	6	15	-	2	0.8	180
GO-Plaster	106	213	6	-	15	2	0.8	165
RHA-GO-Plaster	106	213	6	15	15	2	0.8	165

3.4.1 RHA for thermal comfort

RHA is known for its thermal insulating and pozzolanic properties. This was formerly discussed under Chapter 2. Many studies have shown that RHA provides excellent thermal comfort and provides a strength gain due to its high pozzolanic activity [90, 92]. In order to understand the behavior of the additives in the control sample mix, all compositions were kept constant as the control blend, while 5% from each additive was added.

According to the mix design in under Table 8, the samples were prepared but the workability was slightly reduced with the addition of RHA to the control sample. Hence, batch water was increased by 15%, resulting in 80.5 mL of batch water in the sample to gain the same consistency. This was not quantified but identified through visual inspection. The mixing time remained the same for RHA-Plaster samples.

Further, it was observed that early heat of samples were slightly lower than the control specimens.

3.4.2 GO for strength gain

Literature states that RHA lowers the early strength of the samples specially during the initial 24 -48hour duration, but pozzolanic activity picks up the strength in latter stages (after 7 days). Thus, additives that help regain the lost strength during the initial 24-48hour are required for fast mobility of patients fitted in to casts.

Based on existing literature GO was selected as a suitable candidate to regain and maintain the strength of plaster and to reduce plaster cracking [98].

The aqueous GO solution (10g/L and 4g/L) provided by Ceylon Graphene Technologies (CGT) was added to batch water prior to mixing with the plaster. In GO-Plaster samples fast hydration was observed and 5% more retarder and 10mL of additional batch water were added to maintain the same consistency and total time. Visual observations indicated an increase in porosity of the final sample compared to the control specimens.

Figure 11: 4g/L GO solution obtained from CGT, the pH of GO lies between 2-3

3.4.3 Problems encountered in Phase III

Further, visual inspection showed agglomeration of the GO flakes in the final mix. According to literature this agglomeration of GO flakes after the addition of $CaSO_4$ is due

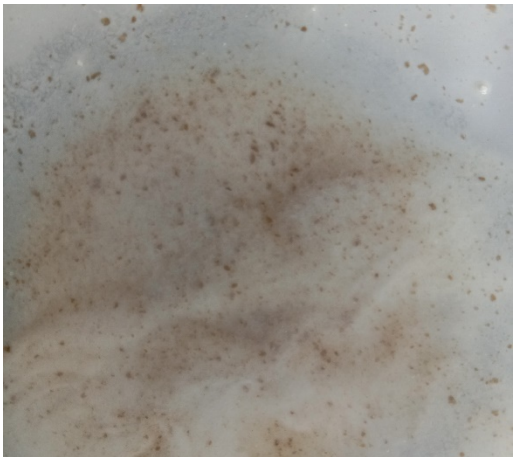

Figure 12: Visual observation of agglomerated GO in $CaSO_4$

to the entrapment of water molecules within the flake. According to *****, the edge planes of GO flakes (which contain Hydroxyl and carboxyl groups) combine with the water molecules from the batch water and fold inside entrapping water molecules. This makes the GO flakes inert in the final sample. Hence, literature suggests that this provides no strength gain and inhibits the action of GO.

This agglomeration of GO in the final slurry was evident in our study too.

3.5 Initial study- Compression testing

For initial testing of the material, the compression test was selected. A modified version of the ASTM C 109/C 109M-2 was carried out to suite the plaster composite testing.

For cube preparation 50mm x 50mm cubes were prepared without any binder addition. The mix design used for the cube preparation is tabulated under Table 8.

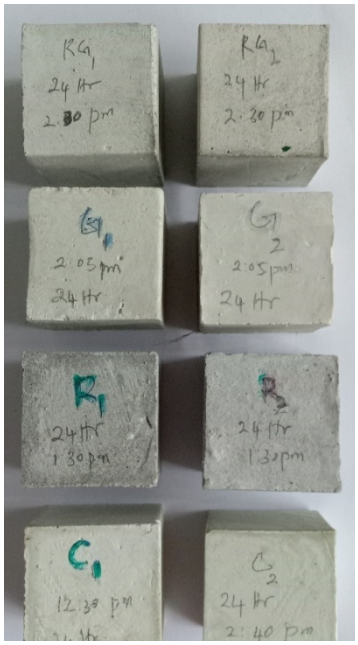

Figure 13: Developed samples for compression testing

The rest of the sample preparation was in lieu with ASTM standards. However, plaster degrades when in contact with water, hence no water curing was carried out. Instead the casted cubes were placed under room temperature (27^0C and 46- 48% relative humidity) for 23 hours, following one hour in an oven at 95^0C to remove all lingering moisture and allow the specimens to completely dry. Lingering moisture in plaster reduces the compressive strength of the specimens.

Upon removal from the oven the surface of the cubes were sanded for any imperfections of the cube faces. The cubes were weighed and measured. The samples were subjected to compression under an average loading rate of 0.05kN/s. Refer Table 9 for obtained results;

Table 9: Compressive strength of tested cubes

Sample Type	Sample Name	Area of cube (mm^2)	Weight of cube (g)	Load to Failure (kN)	Compression Strength (MPa)	Average Compression Strength (MPa)
Control	C1	49x51.5	213.2	15.40	6.103	5.933
	C2	49x51	213.5	14.40	5.762	
RHA samples	R1	50x51	196.3	5.55	2.176	2.030
	R2	50.5x51	201.7	4.85	1.883	
GO samples	G1	51x50	192.2	6.75	2.647	2.735
	G2	51x50	196.3	7.20	2.824	
RHA and GO samples	RG1	51x50	200.6	6.20	2.431	2.275
	RG2	51x50	196.5	5.40	2.118	

(5% each)						

Based on the results obtained it is clear that the control sample performs better in compressive strength compared to other specimens.

RHA plaster samples showed a 65.8% decrease in overall compressive strength, while GO plaster samples showed a 53.9% decrease in overall compressive strength. The RHA-GO-Plaster samples showed a 61.7% decrease in the compressive strength. Thus, it is evident that none of the samples performs better than the control as per the mix design under Table 8. Only a slight weight reduction was observed in the samples compared to the control.

3.6 Altering the pathway – Phase IV

Based on the results obtained under phase III, it was clear that neither GO and RHA has improved the strength of the specimen nor has it retained the compressive strength compared to the control.

Literature suggests that GO dissipated in water and mixed into concrete or any other material has the tendency to trap water molecules inside the flake [105] and agglomerate cutting down the performance of GO. This is can be seen in $Ca(OH)_2$ and even in $CaSO_4$ environments. Thus, the study suggests the use of a PCE based superplasticizer to eliminate the GO agglomeration.

3.6.1 Superplasticizer for workability and strength gain

According to literature suggestions and superplasticizers available in Sri Lanka; a Poly Carboxylic Ether-based superplasticizer with high compacting ability named

HYPERCRETE was obtained from a commercial supplier. The TDS of HYPERCRETE states that the product is nontoxic and comes with its own inhibitor, which is Glucose. Thus, the use of the Ammonium borate inhibitor in the final mix would further lengthen the setting time. Glucose is derma friendly compared to Ammonium borate. Thus, the Ammonium based inhibitor was replaced by the superplasticizers' inhibitor. The superplasticizer composition was at 2% of the plaster composition as per the industry standard for cement. The material is of high cost and can highly improve the workability and flow rate of the resulting slurry.

The mix design was altered based on all these observations and findings (Note: the amount required for two samples of each category are provided here to avoid any material wastage, refer Table 10 for the required composition);

Table 10: Altered mix design incorporating PCE and excluding Ammonium Borate

Specimen Category	α- $CaSO_4$ (g)	β- $CaSO_4$ (g)	K_2SO_4 (g)	RHA (g)	GO (10g/L)	PCE (mL)	H_2O (mL)
RHA-Plaster	94	188	3	15	-	5.64	75
GO-Plaster	94	188	3	-	15	5.64	60
RHA-GO-Plaster (5% additives each)	94	188	3	15	15	5.64	60
RHA-GO-Plaster (2.5% additives each)	94	188	3	7.5	7.5	5.64	60

The Phase III mix design was used for the control mix and the new mix design was developed through trials to avoid any material wastage. It can be seen that with the use of superplasticizer shows a significant reduction of the required material along with the total batch water requirement. All preparation methods were kept constant as previously followed, including the modified ASTM C 109/C 109M-2 and room conditions maintaining a tolerance range of ± 5% to maintain consistency of results. The superplasticizer was added to the batch water, not directly into the dry plaster mix (this was recommended by the supplier, previous literature and according to the industrial practice). In addition of GO, GO was suspended in a water-PCE solution prior to addition to the dry plaster mix.

During sample preparation the following observations were made;

1. The control sample was thicker in consistency than the remaining – had a creamy consistency. Heat dissipation was observed from the samples upon hardening, increased temperature of the molds. Setting time was between 6-10 minutes. (Tested under phase III)
2. RHA-plaster samples had a moderately thick slurry, low heat dissipation than the control during setting. Setting time was slightly higher than the control (8-15 minutes)
3. GO-RHA-plaster samples has a similar consistency to that of the RHA-plaster in both 5% additives and 2.5% additive scenarios. Heat dissipation was similar to that of RHA-plaster samples but the setting time was between (10-18 minutes)

4. GO-plaster samples showed a higher watery consistency than the rest of the samples. This can be due to GO+ superplasticizer action and took a considerably higher time to set (25-30 minutes). The heat dissipation was almost similar or higher than that of the control samples. There was no agglomeration of GO observed upon addition into the water-superplasticizer solution and within the final slurry.

After subjecting to compression, the following results were obtained;

Table 11: Compression test results of the samples developed under phase IV

Sample Type	Sample Name	Area of cube (mm^2)	Weight of cube (g)	Load to Failure (kN)	Compression Strength (MPa)	Average Compression Strength (MPa)
GO samples	$R1_4$	50x50	218.4	24.85	9.55	9.85
	$R2_4$	49.5x50	217.9	25.1	10.14	
RHA samples	$G1_4$	51x51	239.6	37.05	14.25	14.62
	$G2_4$	50x50	240.0	37.45	14.98	
RHA and GO samples (5% additives each)	$RG1_4$	52x50	224.8	28.25	11.08	11.14
	$RG2_4$	51.5x50.5	224.6	29.10	11.19	
RHA and GO samples (2.5% additives each)	$RG3_4$	51x51	228.2	19.10	7.34	7.81
	$RG4_4$	49.5x50	227.5	20.50	8.28	

The control sample under phase III showed a compression strength of 5.93 MPa. In comparison GO samples showed 66.1% increase in compression strength while the RHA samples showed a 146.54% increase in strength gain. While RHA-GO-plaster samples (5% additives each) showed a compression strength gain of 87.85% and the 2.5% additives category showed a gain of 31.7%. Based in the results it can be seen that RHA-plaster performs better without GO addition.

3.7 Comparison of results obtained in Phase III and Phase IV

The main difference between phase III and phase IV is the replacement of the inhibitor with superplasticizer and reduction of the material quantities in the mix design. This shows that superplasticizer optimizes the use of material, while improving the workability of the resulting mix.

Table 12: Comparison between phase III and phase IV results for modified blends

Sample category	Phase III	Phase IV	Percentage increase
RHA-plaster	2.030	14.62	620.2%
GO-plaster	2.735	9.85	260.15%
RHA- GO plaster (5%)	2.275	11.14	389.7%

The control sample was not prepared using superplasticizer addition and the results obtained falls within the literary findings for orthopedic plaster which lies between 5-6 MPa. Thus, there is a higher scope for replacement of plaster using sustainable additives. Considering the economic feasibility of material, ease of acquisition and preparation,

setting times and the promise of the results obtained, RHA was identified as the additive to progress with for the final study.

3.8 Chapter Summary

The comprehensive studies conducted under this chapter have developed and optimized the control plaster mix, while exploring the incorporation of sustainable fillers such as Rice Husk Ash (RHA) and Graphene Oxide (GO) to enhance performance. The phased approach allowed systematic identification and resolution of challenges, leading to significant improvements in material properties and workability.

The initial phase highlighted the limitations of using Dichloromethane (DCM) due to its toxicity and the agglomeration issues when using PVA crystals. These challenges were effectively addressed under Phase II, by replacing DCM with a water-based system incorporating an ammonium borate inhibitor and switching to commercial PVA glue. However, the introduction of RHA and GO in Phase III revealed a trade-off between thermal comfort and compressive strength, with both additives initially reducing the plaster's mechanical performance.

The breakthrough came in Phase IV with the introduction of a polycarboxylic ether (PCE)-based superplasticizer, which not only improved workability but also mitigated GO agglomeration and enhanced the overall strength of the plaster. The results demonstrated a significant increase in compressive strength, particularly for RHA-plaster samples, which showed a 146.54% improvement than the control. This underscores the potential of

RHA as a sustainable filler for orthopedic plaster, offering both thermal comfort and strength gain.

The comparative analysis between Phase III and Phase IV clearly illustrates the transformative impact of the superplasticizer, with RHA-plaster emerging as the most promising sustainable filler for further development. Its economic feasibility, ease of acquisition, and superior performance make it a viable alternative to traditional plaster formulations.

In conclusion, this chapter has provided the foundation for the development of sustainable, mechanically strong and thermally comfortable orthopedic plaster. The findings address the limitations of conventional materials and open new avenues for incorporating eco-friendly additives for fracture immobilization. Chapter 4 focuses on refining the most suitable RHA replacement percentages that balance thermal comfort and compressive strength.

CHAPTER 4- DEVELOPMENT OF RHA MODIFIED PLASTER BLENDS

4.1 Introduction

Following the preliminary investigation under Chapter 3, on the development of the control sample and selection of RHA as a suitable filler, the final samples were developed. Replacement of a series of percentage compositions of plaster with RHA, was carried out in this chapter to selected the most suitable RHA replacement percentages for the experimental study under Chapter 5.

4.2 Selecting the RHA replacement percentage

Literature states that different RHA replacements have been added to plaster panels designed for thermal comfort [106]. Most mix designs use replacements values above 2%-below 50%, as higher RHA replacements largely compromise the compressive strength. This study aims to develop a material of high thermal comfort, compared to existing orthopedic plaster as the threshold for strength and thermal comfort. The replacement percentages mentioned below were selected for sample preparation;

I) 0% replacement – control

II) 5% RHA replacement

III) 10% RHA replacement

IV) 15% RHA replacement

V) 20% RHA replacement

VI) 25% RHA replacement

VII) 30% RHA replacement

VIII) 35% RHA replacement

All sample mix designs were prepared according to Table 10, maintaining the water and other additives constant, with only a percentage of the total plaster composition being replaced by the aforementioned RHA % by weight.

The mix design for RHA replacement blends is tabulated below.

Table 13: Mix design for different RHA modified plaster samples

Sample category		**Control**	**5% RHA**	**10% RHA**	**15% RHA**	**20% RHA**	**25% RHA**	**30% RHA**
Material (g)	α- $CaSO_4$	32.8	31.16	29.52	27.88	26.33	24.6	22.96
	β- $CaSO_4$	65.6	62.32	59.04	55.76	52.46	49.2	45.92
	K_2SO_4	1.5	1.5	1.5	1.5	1.5	1.5	1.5
	RHA	0	4.92	9.84	14.76	19.7	24.6	29.52
	PCE	1.97	1.97	1.97	1.97	1.97	1.97	1.97
	Water	26.3	26.3	26.3	26.3	26.3	26.3	26.3

Since, cubes were casted and no plaster bandages were tested during this stage no binders were included in the mix design.

According to Figure 15, the developed samples visually showed a darkening of the mixture at higher RHA replacement quantities along with an expansion in volume.

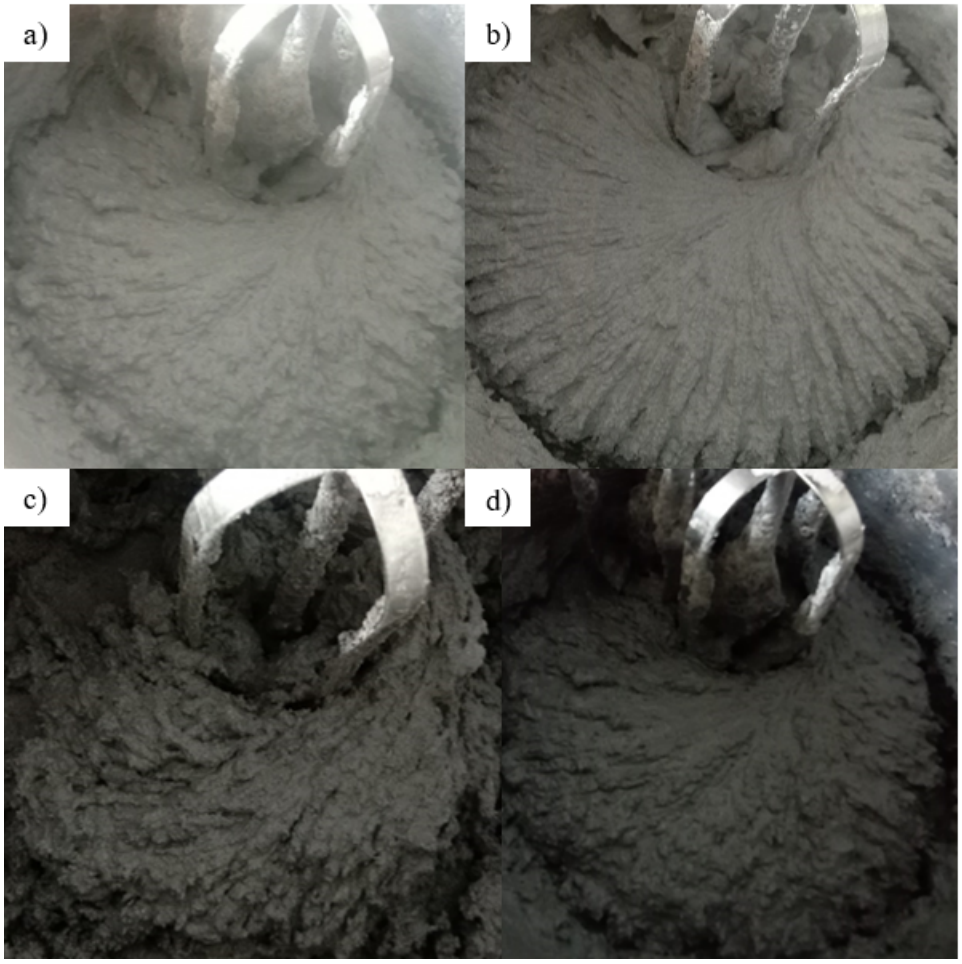

Figure 14: The variation of color with increasing additions of RHA a) 5% RHA b)10% RHA c)15% RHA d)20% RHA

4.3 Compression testing to select the optimum RHA replacement percentages

To decide on the optimum RHA replacement percentages for further analysis, the samples were subjected to compression. Three samples of each category were subjected to compression to obtain the average compression strength per sample category. A modified version of the ASTM C 109/C 109M-2 was carried out to suite the plaster composite

testing, as performed under the preliminary investigation. The samples were tested after 7days of curing at room temperature.

Generally, patients fitted to plaster of Paris (POP) casts are dispatched after 2-3 hours of cast application. However, for testing of material characteristics and to allow proper material integration in the micro level; i.e., to form needle like plaster crystals and for optimized RHA interactions with $CaSO_4$, the samples were left for 7 days at room temperature of 23-25℃ at 75-94.2% relative humidity.

Table 14 elaborates the compression test results and the weight characteristics of the tested samples;

Table 14: Compression test results and weight of different RHA replacement percentages

RHA % in sample	Weight (g)	Failure Load (kN)	Surface area (mm^2)	Compressive Strength (Mpa)	Volume (mm^3)	Density (g/mm^3)	Percentage reduction in density	Percentage variation in compressive strength
0%	235.50	14.96	2523.5	5.930	126175	0.001866	0.00%	0.00%
5%	231.55	23.90	2575.5	9.288	128775	0.001798	3.66%	56.49%
10%	219.95	16.55	2550	6.490	127500	0.001735	7.57%	9.45%
15%	217.05	15.50	2550	6.079	127500	0.001702	8.79%	2.50%
20%	201.00	13.05	2500	5.220	125000	0.001608	13.85%	-11.97%
25%	205.30	06.35	2450	2.592	122500	0.001676	10.21%	-56.29%
30%	185.00	03.00	2499.5	1.200	124975	0.00148	20.69%	-79.76%

Table 14 shows that the compressive strength of samples are above the threshold (control sample value of 5.930 MPa) for 5%, 10% and 15% replacements of RHA. However, replacements from 20% RHA show -11.97% to -79.76% reduction in overall compressive strength compared to the control.

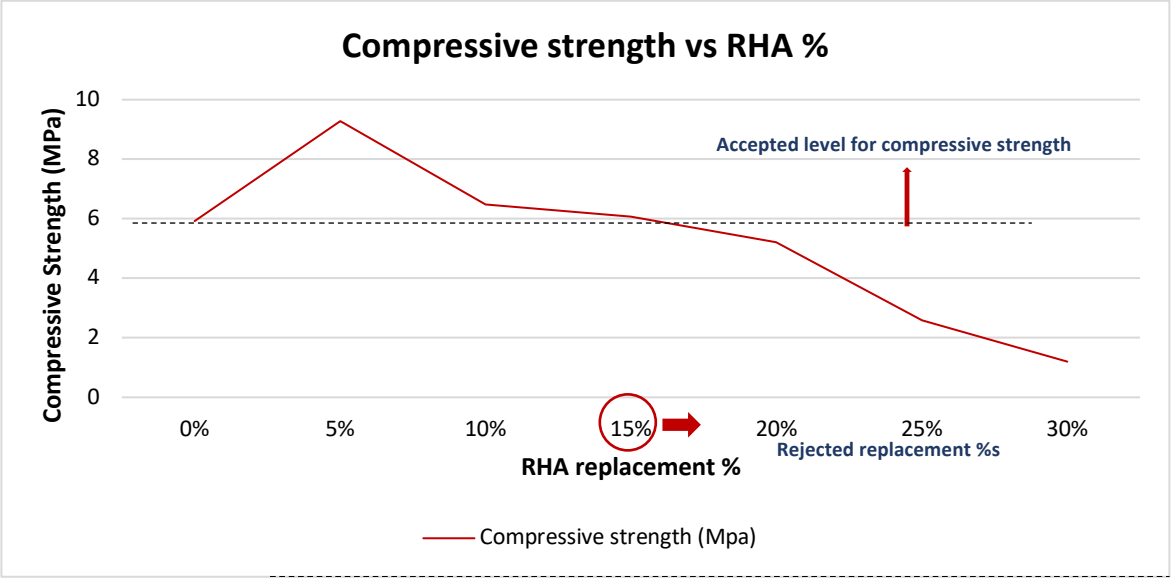

Figure 15: Variation of compressive strength with different RHA percentages

Figure 16, graphs the variation of compressive strength for the tested samples and the line of threshold below which the RHA replacement %s are rejected for this study. It is evident that 5% replacement of RHA shows a 56.49% strength gain after which the compressive strength gradually declines.

Table 14 shows, that as RHA replaces POP by weight, there is a clear reduction in sample weight. This causes a reduction in the material density, by 20.69% when 30% RHA replacement was carried out. Thus, making the overall sample light in weight. The weight and density variations with increasing RHA % are graphically shown by Figures 17 and 18.

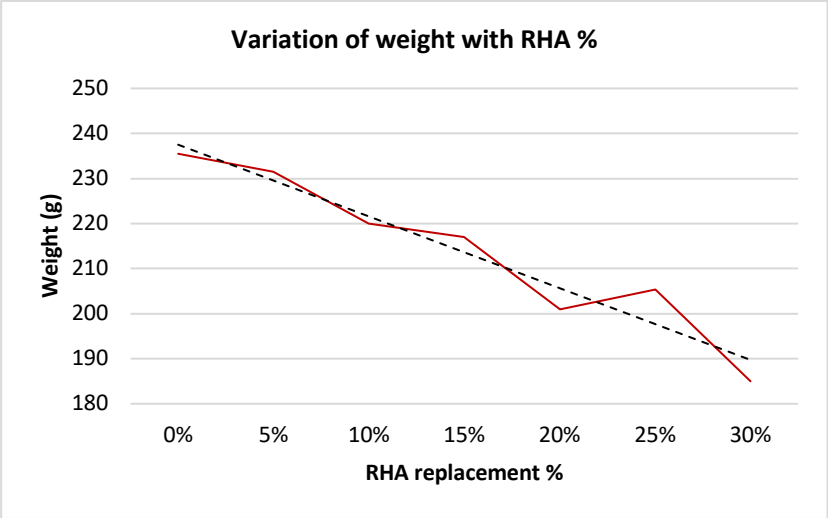

Figure 16: Variation of weight with different RHA percentages

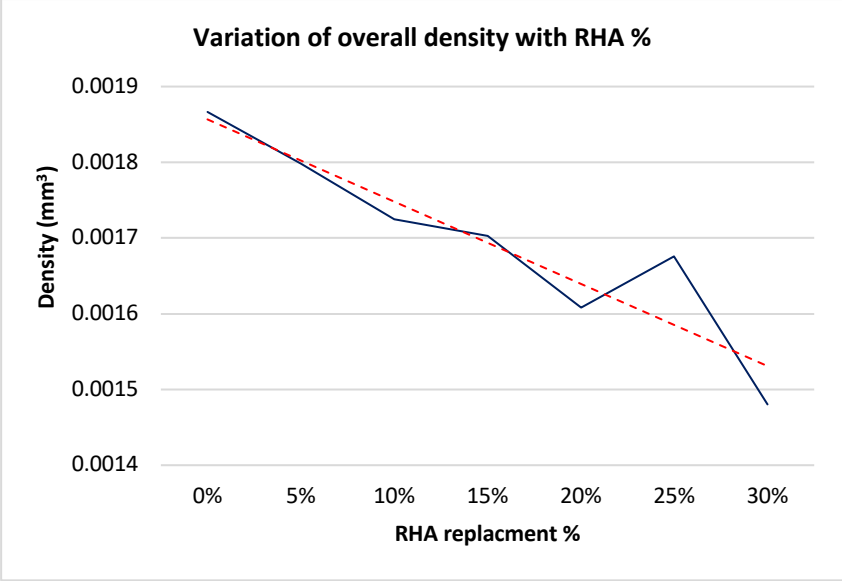

Figure 17: Variation of density with different RHA percentages

4.4 Chapter summary

This chapter focused on the development and optimization of Rice Husk Ash (RHA)-modified plaster blends, building on the findings of Chapter 3. The primary objective was to identify the most suitable RHA replacement percentages that balance thermal comfort and compressive strength, ensuring the material meets the requirements for orthopedic applications.

A systematic approach was adopted, testing RHA replacement percentages ranging from 0% (control) to 30% composition by weight. The results revealed a clear trend: up to 15% RHA replacement, the compressive strength of the plaster remained above the threshold value of 5.930 MPa, with the 5% RHA replacement showing a significant 56.49% increase in strength. However, beyond 15% RHA replacement, the compressive strength declined significantly, with 30% RHA replacement resulting in a 79.76% reduction in strength compared to the control.

In addition to strength, the study highlighted the impact of RHA on the density and weight of the plaster. As RHA replacement increased, the samples became lighter, with a 20.69% reduction in density at 30% RHA replacement. This reduction in weight is advantageous for patient comfort, but the trade-off in strength must be cautiously considered.

The findings from this chapter underscore the importance of optimizing RHA replacement percentages to achieve a balance between thermal comfort, weight reduction, and mechanical performance. Based on the results, RHA replacements of 5%, 10%, and 15%

were identified as the most promising mix designs for further investigation under Chapter 5, where their thermal and mechanical properties will be evaluated.

In conclusion, this chapter successfully demonstrated the potential of RHA as a sustainable filler for orthopedic plaster, to enhance thermal comfort and reduce material weight without significantly compromising strength. The insights gained here lay the groundwork for the development of advanced, eco-friendly plaster blends that meet the dual demands of patient comfort and clinical efficacy.

CHAPTER 05- PERFORMANCE EVALUATION OF RHA BASED ORTHOPEDIC PLASTER

5.1 Introduction

Chapters 3 and 4 methodically elaborates the process of development of the mix design for the study. Under this chapter the mix design for RHA modified orthopedic plaster (i.e, replacing a % of POP from the control mix with RHA) was developed into bandages/paste and tested for their material characteristics, mechanical and thermal properties. Bandages bearing the modified mix was made up of a cotton base and chosen to closely mimic the existing commercial POP bandages.

For performance evaluation RHA modified plaster bandages were tested for both mechanical and thermal performance, along with a microstructure analysis. Initially, to understand how the microstructure behaves, Scanning Electron Microscopy (SEM) imaging and Brunauer-Emmett-Teller (BET) surface area was carried out, followed by mechanical and thermal performance testing;

- *Microstructure analysis and imaging*

i) Scanning Electron Microscopy (SEM)

ii) BET surface area

- *Mechanical performance evaluation*

i) Weight and density

ii) Bead test

iii) Setting time

iv) Compression strength

v) Wet crush strength

vi) Tensile strength

- *Thermal performance*

i) Early heat of reaction – isothermal calorimetry

ii) Thermal conductivity and thermal effusivity

5.2 Final mix design and specimen development

Based on chapters 3 and 4, the mix design for the samples were finalized as below;

Table 15: Finalized mix design for samples, including RHA modified blends

Material used (g)	**Sample category**	**Control (0% RHA)**	**5% RHA**	**10% RHA**	**15% RHA**
α- $CaSO_4$		85.5	81.26	76.95	72.67
β- $CaSO_4$		171	162.45	153.9	145.35
K_2SO_4		6	6	6	6
RHA		0	12.82	25.65	38.47
Water		216	216	216	216
Superplasticizer (2% by weight of total $CaSO_4$)		5.13	5.13	5.13	5.13
PVA		30	30	30	3
HPMC		3	3	3	3

(The mix was coated on to coat 2.5m of cotton bandage)

In developing the final samples for performance and thermal analysis the samples were developed as large batches, following the process described under phase II (Chapter 03).

Initially, $\frac{1}{3}$of the total batch water was used to prepare the binder paste (PVA +HPMC), while super plasticizer was added and stirred into the remaining $\frac{2}{3}$. A mechanical stirrer was used in the mixing process.

Upon preparation of the binder paste, K_2SO_4 was added and stirred for 5 minutes, after which RHA was added and mixing continued for another 2 minutes. Finally, the plaster mix was added along with the remining water. Total mixing time was 10-12 minutes with mixing to be maintained below 5 minutes after plaster addition, to reduce any risk of hardening before coating. The resulting slurry was maintained at a creamy consistency to ensure homogeneity of the mixture.

2- ply cotton plasters with a thread count of 46 threads per square inch, were coated with the mix, using palette knives to gain an even coating on either side of the bandage. The bandages were air dried at room temperature (25-27°C) for a day. Dried plaster rolls were kept wrapped in plastic wrap to avoid hydration of the plaster when in contact of water/ water vapor.

Figure 18: Prepared bandage samples of the control

5.3 Preparation of samples for testing

The prepared bandages were maintained at 2mm thickness each. Any excess plaster was filled off using 80 grit sandpaper. This was done to minimize uneven distribution of plaster in the bandage. All samples were left to air dry for 7 days under the same room conditions to ensure proper drying of all layers.

3 samples were prepared from each category per test and averaged to ensure uniformity of results.

(Specimen preparation for each test varies and is explained under the respective testing procedure)

5.4 Microstructure Analysis

5.4.1. Investigation of microscopic characteristics of the material -SEM

Introduction:

SEM (Scanning Electron Microscope) microstructure analysis plays a crucial role in enhancing the understanding of the microstructural characteristics of plaster and RHA-plaster composites. The importance lies in the closer examination of the crystal morphology and interparticle bonding within the plaster composite matrix, providing valuable information on the cast's mechanical properties, such as strength and durability. Carrying out a SEM analysis early on for a study provides good visual observations on how the material behaves.

Additionally, SEM can reveal the presence of any defects, inclusions, or irregularities in the composite that may impact its performance during orthopedic applications and it’s mechanical and thermal characteristics. By uncovering these microscopic details, SEM microstructure analysis contributes to the optimization of plaster of Paris and Plaster-RHA

composite casts, aiding in the development of more robust and reliable orthopedic solutions for patient care.

Sample preparation and Test Method:

Two types of samples were prepared from each category;

1. Hardened plaster blends
2. Bandage samples

The bandage specimens were cut out from the prepared bandage rolls, wetted through water immersion as in plaster layup and allowed to dry at room temperature for 7 days.

For the latter, the paste was allowed to hardened at room temperature for 7 days similar to the bandage samples.

Before subjecting to testing the surfaces were smoothened using sandpaper to remove surface irregularities.

The Hitachi FlexSEM 1000 was used to conduct the microstructure analysis. The prepared samples were positioned as show under Figure 19.

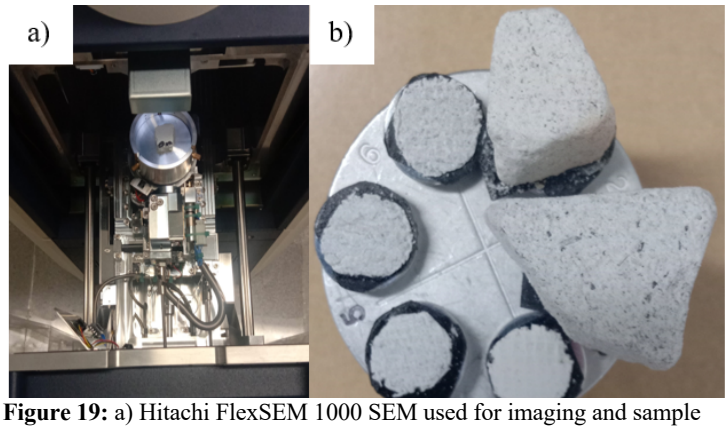

Figure 19: a) Hitachi FlexSEM 1000 SEM used for imaging and sample positioning b) Sample positioning of observation tray

Results and Analysis:

Control Sample

-Microstructure of the paste

Literature states that α- $CaSO_4$ hardens to form long needle like crystals, while β- $CaSO_4$ forms short sturdy crystals [100, 107].

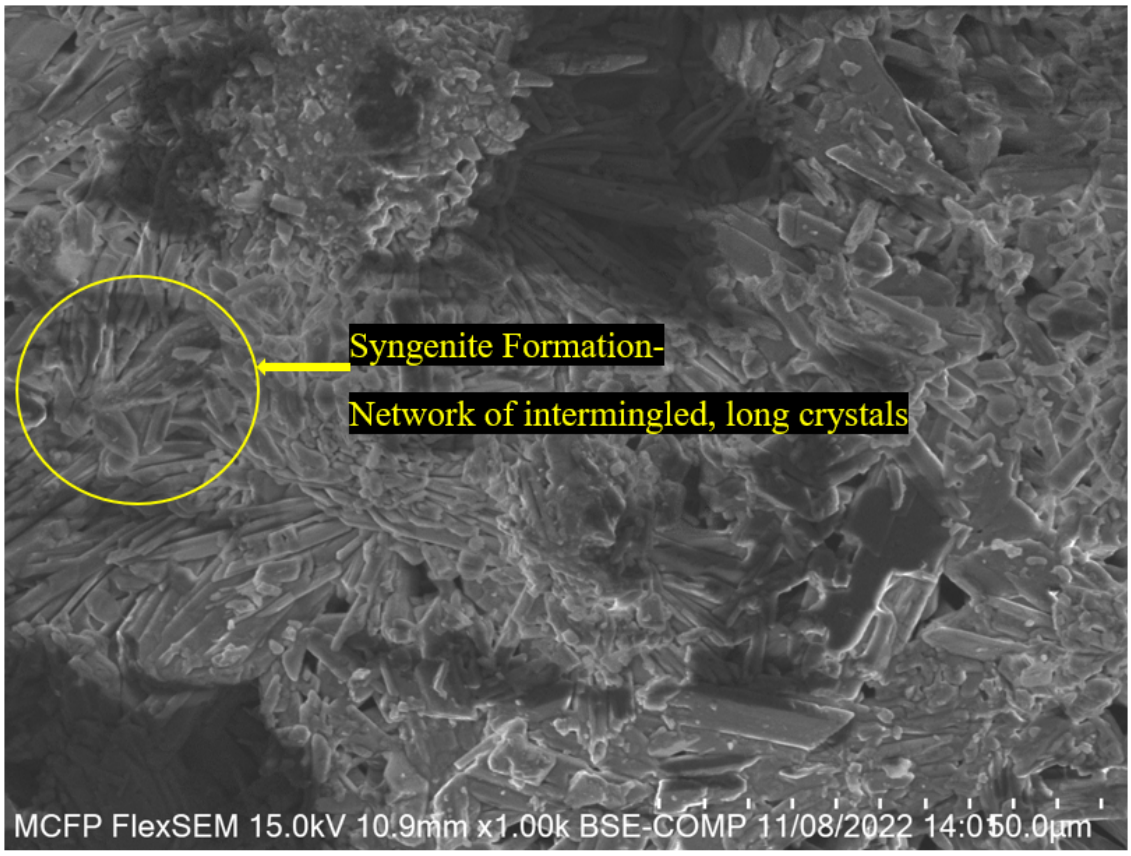

Figure 20:SEM image of the control sample at x 1000, showing syngenite formation sites

As the prepared samples comprise of a higher % of β- $CaSO_4$, theoretically shorter sturdy crystal formation has to be observed.

However, an intermediate between these were found in the observed specimen, with nucleation points from which the crystallization radiates outwards. A network of intermingled and shorter crystals of (10-15µm) were observed as shown in Figure 20.

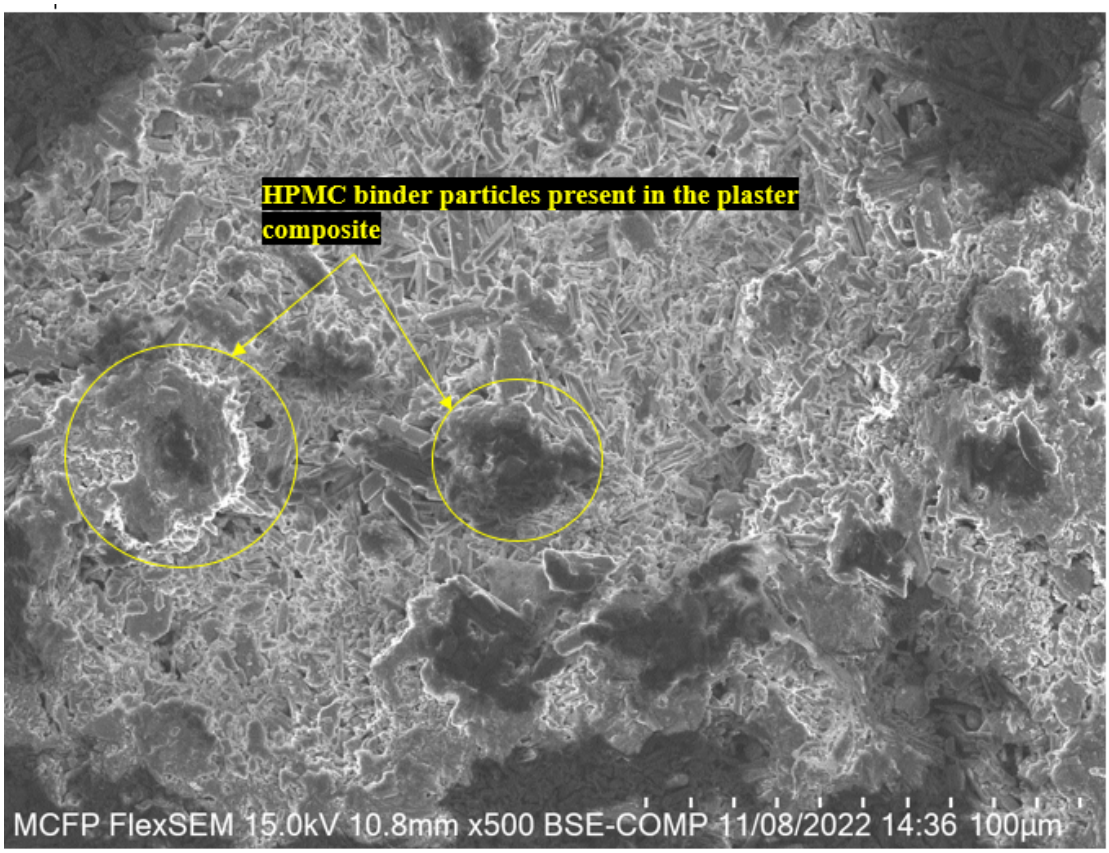

Figure 21: HPMC binder particle agglomerates at x 500

According to Shen et al. [108], nucleation points and spherulitic crystal formation was due to the concentration of K_2SO_4 in the mix. K_2SO_4 was added as an accelerator and nucleator. K_2SO_4 together with Ca_2SO_4 forms a complex compound called $K_2Ca(SO_4)_2.H_2O$ or syngenite. Syngenite formation improves the regularity of crystal packing and forms a denser microstructure.

Until all K^{2+} are used up, the syngenites precipitate. Afterwards, the remaining $CaSO_4.2H_2O$ precipitates outwards from the syngenite centers, in short and sturdy crystals due to the excess presence of β- $CaSO_4$ in the mix. As the mixes have 2% K_2SO_4, the syngenite sites are not highly visible in a majority of SEM images.

However, SEM analysis of the control bandages provides better morphology of the crystallization, crack propagation and presence of voids in the final mix.

The paste blends were used for thermal analysis of the composite and the bandage specimens were used in mechanical performance analysis. Thus, it is crucial to analyze the microstructure of the bandage samples.

-Microstructure of plaster bandages

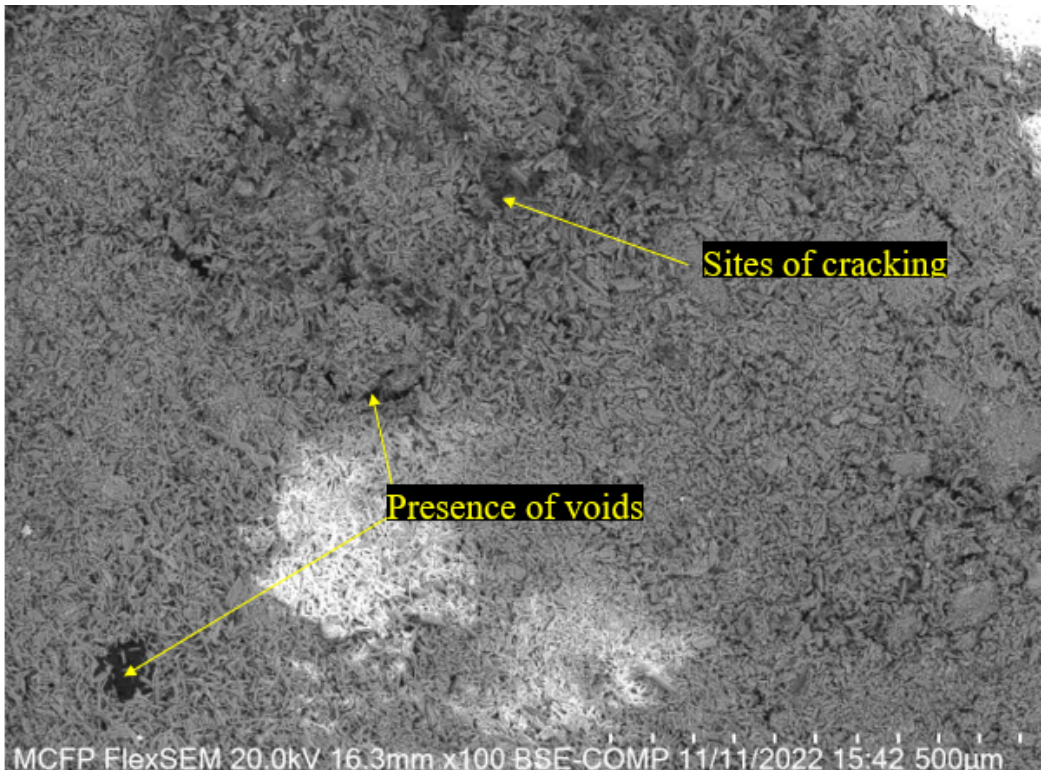

Figure 22: Presence of voids and sites of cracking in plaster bandage specimens at x100

SEM analysis of the plaster bandages depicted short sturdy crystal formation of β- $CaSO_4$ hydration as well as an abundance of microcracks on the surface along with the presence of voids.

This microcracking results in the "wick effect", which translates to thermal conductivity, heat transfer and breathability of the final cast. However, the surface appeared to be highly textured and inhomogeneous, with HPMC binder particles forming large agglomerates. This inhomogeneity has caused cracking at inter transition zones and void formation. HPMC binder agglomeration was only detected in control samples.

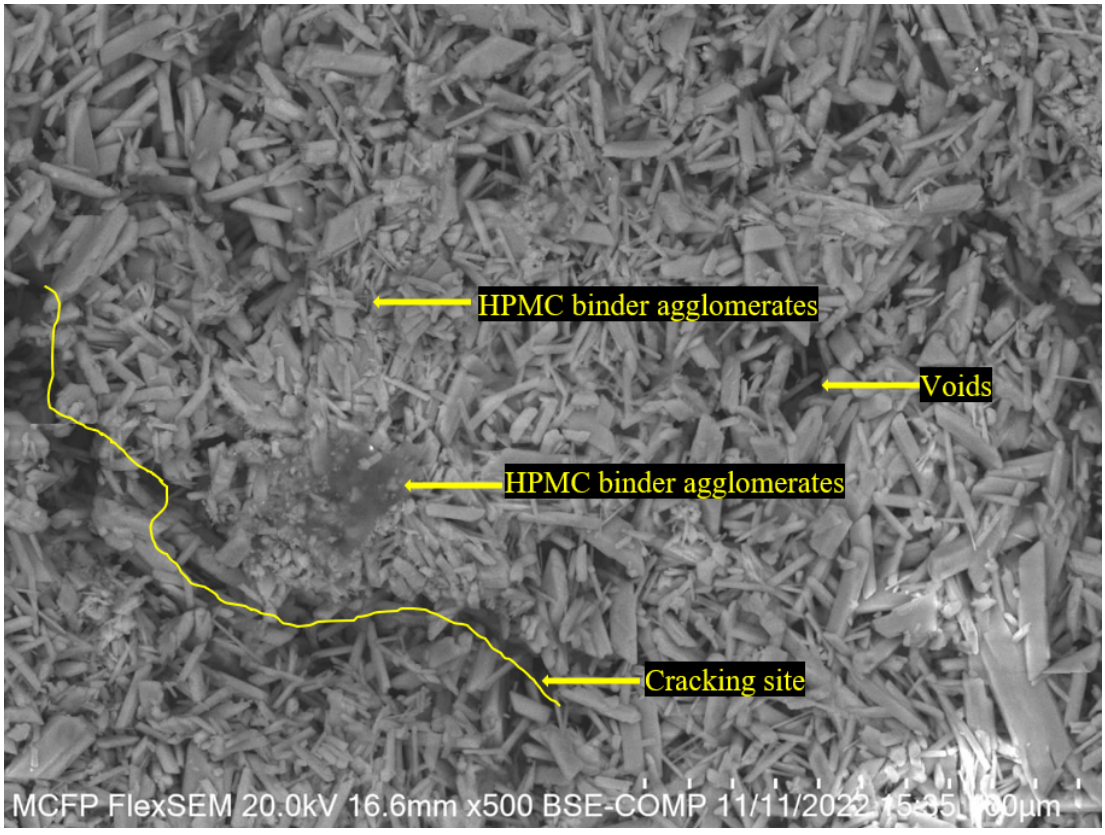

Figure 23: HPMC agglomeration and void presence of plaster bandage samples at x500

At higher magnifications of x500 the crystal formation, cracking and voids were highly visible (Refer Figure 23). The Microstructure imaging of the control showed that crystal formation was predominantly made of short sturdy crystals in disarray. Crack lengths > 50µm on average were detected. The inhomogeneous distribution of agglomerated binder was strewn around the matrix. Syngenite formation sites were barely visible in plaster bandage samples.

However, the SEM images depicted that majority of $CaSO_4$ remain hydrated with gypsum formation, with an abundance of microcracks due to evaporation of water after plaster setting.

5% RHA modified samples

-Microstructure of the paste

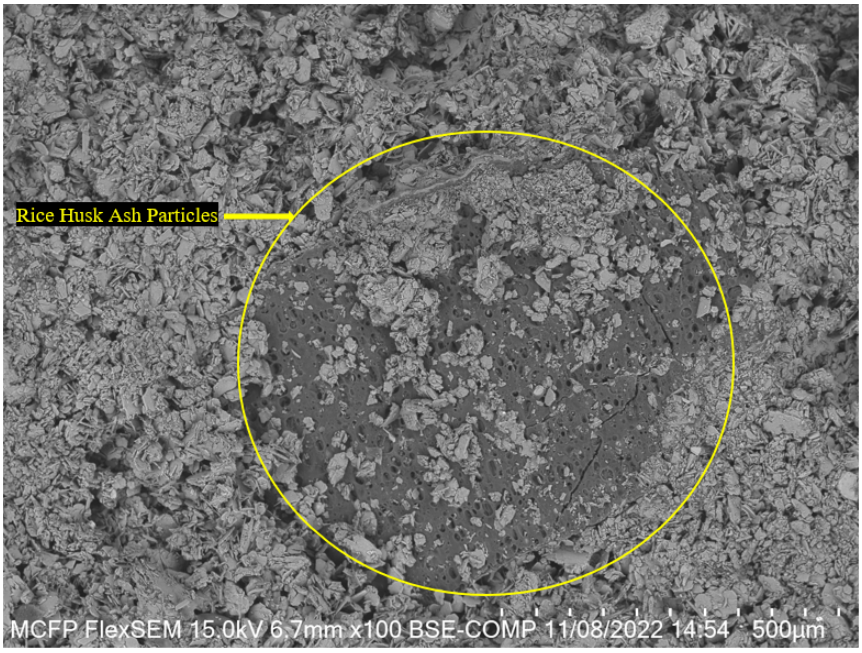

Figure 24: Large RHA particle detected in 5% RHA modified blends, showing $CaSO_4$ crystallization on top of the particle at x100

According to Figure 24, large RHA particles were visible. However, on closer observation i.e, zooming in on the RHA particle, it was evident that $CaSO_4$ crystallization had occurred on top of RHA particles. In most locations RHA particles were engulfed by plaster crystals.

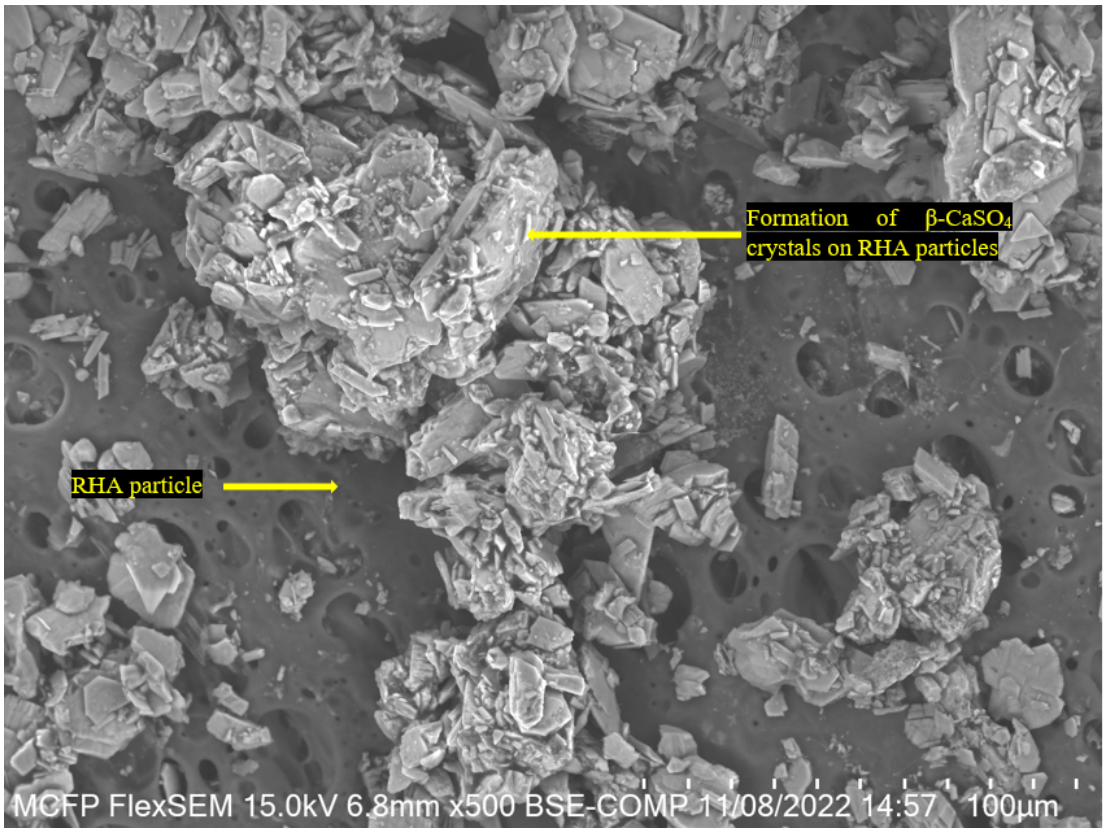

Figure 25: Closer observation on the crystallization on top of RHA particles

The β-$CaSO_4$ crystals formed on top of RHA particles, were not similar to those observed in the control sample.

The crystals appeared disoriented and formed on top of each other, forming a flake like structure. This could be mainly due to inadequate hydration. Previous studies conducted

by Khalil et al. [109], showed that in the presence of PVA, plaster crystals mimic a flake like structure composed of short sturdy crystals. A similar observation was found in all RHA modified samples.

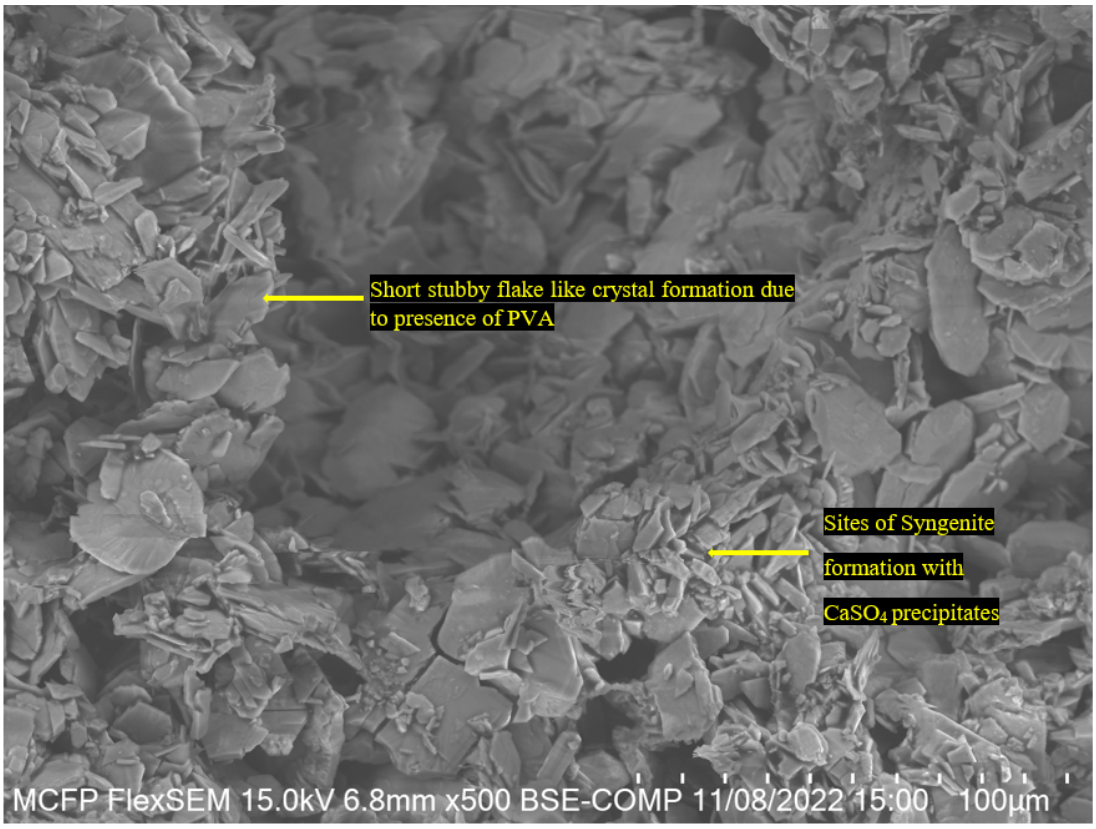

Figure 26: Short sturdy flake like crystal formation in RHA blends, these engulf the RHA particles as RHA entraps water the crystals require for formation

The samples were left to dry for 7 days, this clearly showed that RHA particles have entrapped water from the mix. However, at 7 days the entrapped free water moves out of the RHA particles as the sample dries and these were obtained by unhydrated $CaSO_4$ in the matrix. Thus, formation of β-$CaSO_4$ crystals on top of the RHA, engulfing them.

Syngenite formation sites were barely visible in 5% RHA samples, due to secondary hydration of the $CaSO_4$ with free water entrapped by RHA and binder. Needle like $CaSO_4$ crystals are found deep within the mix according to Figure 26.

-Microstructure of 5% RHA modified bandages

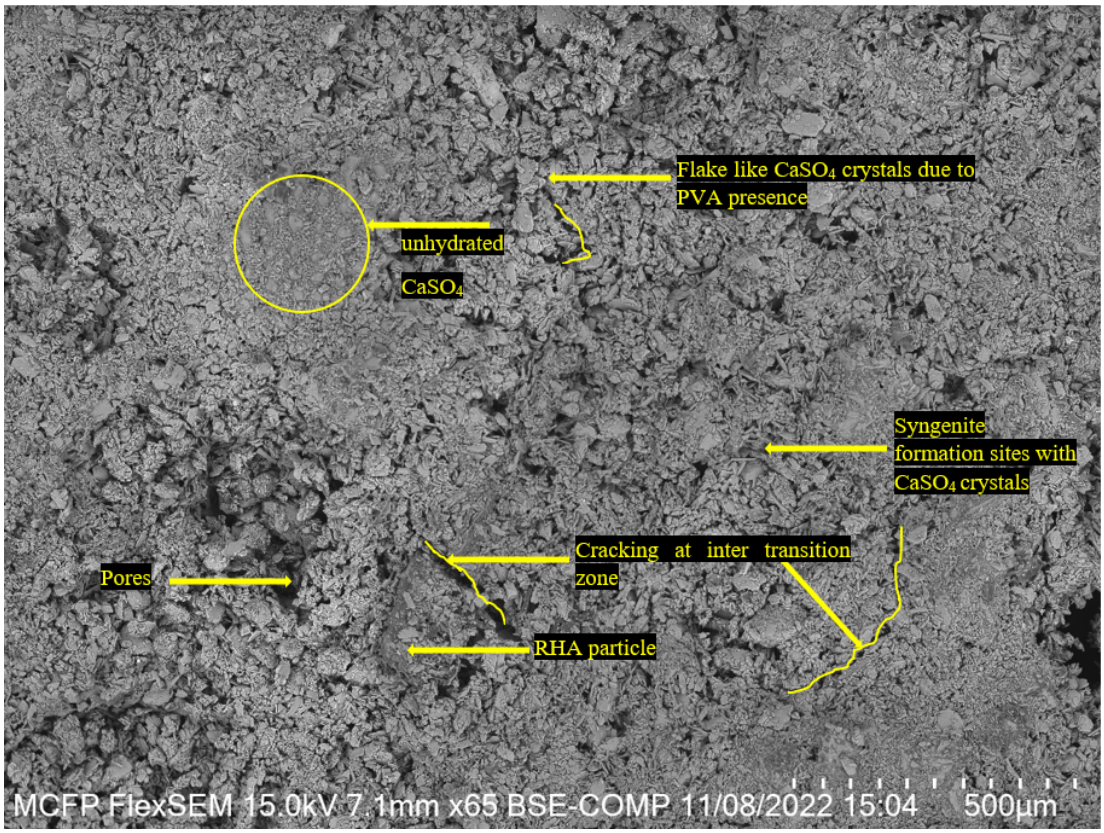

Figure 27: Unhydrated $CaSO_4$ sites, flake like crystal formation, Syngenite formation sites and cracks on 5% RHA modified bandages samples observed at x 65

The 5% RHA modified bandages depicted high irregularity in the paste. Zones of unhydrated $CaSO_4$ were visible, with cracks lengths of 200-500µm or more. Majority of the cracking was localized at inter-transition zones of RHA particles and the plaster matrix.

Larger pores or voids were seen compared to the control sample. However, cracks per unit area were lesser in the 5% RHA samples compared to other RHA modified samples. RHA particles present per unit area were lower than the 10% and 15% RHA modified samples. Thus, cracking at inter-transition zones were much lower than the other two modifications.

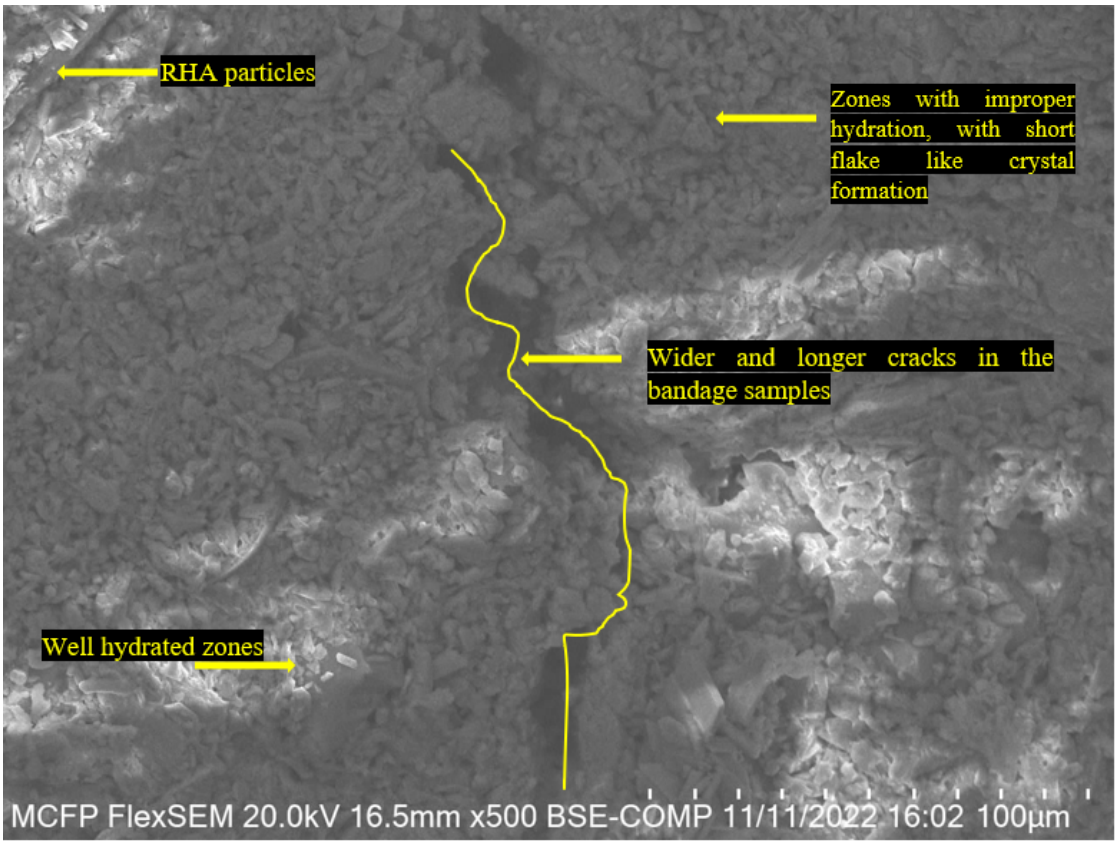

Figure 28: RHA particle detection sites, larger crack widths and partially hydrated zones of plaster in 5% RHA modified blends x 500

At magnifications of x500, it was evident that the crack widths were between 10-30µm at some regions. Although larger pores and voids were present compared to the control, the micropore presence per unit area was much lower in 5% RHA modified samples than the control. Well hydrated zones showed syngenite formation and needle like crystals. Zones

that were hydrated by free water entrapped by RHA and binder, showed disoriented flake like crystals. Thus, forming a much denser structure than the rest.

10% RHA modified samples

-*Microstructure of the paste*

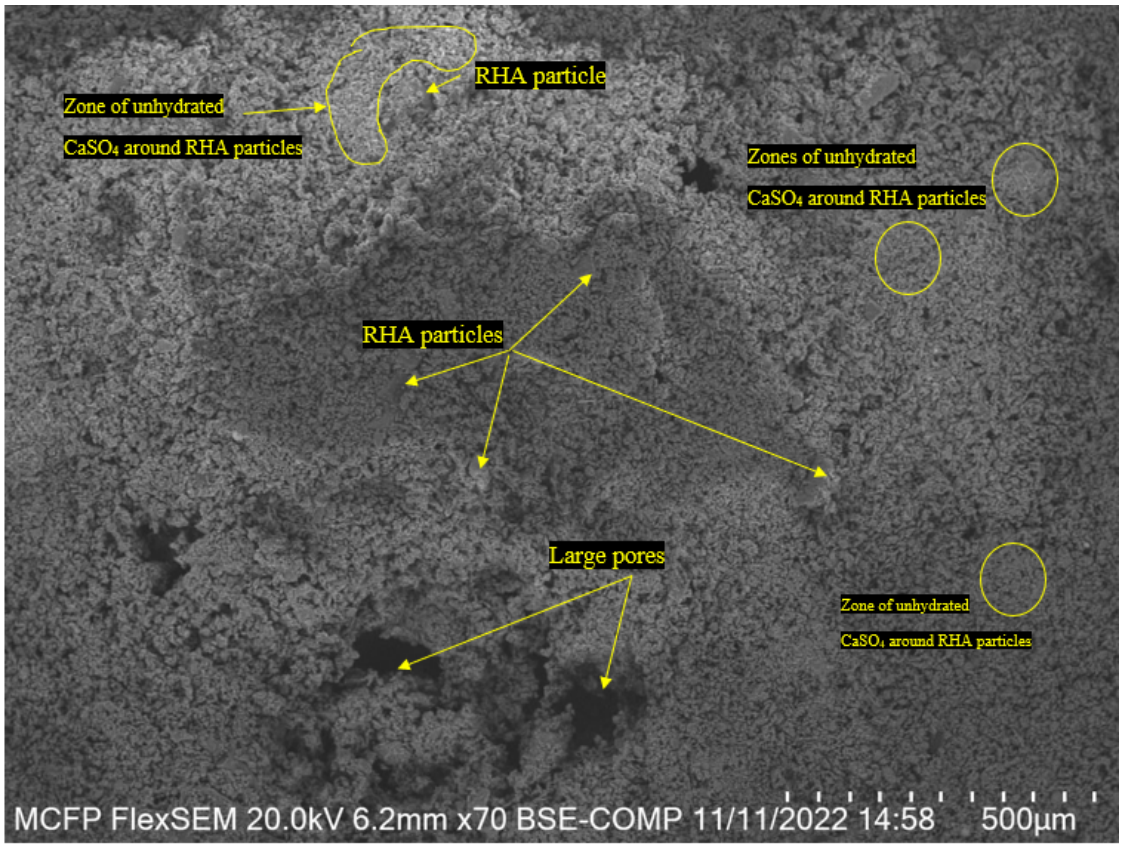

Figure 29:Microstructure of the 10% RHA modified paste including unhydrated zones and RHA distribution at x70

In observing the microstructure of the 10%RHA modified samples, it was evident that a higher degree of unhydrated $CaSO_4$ was present compared to the control and 5% RHA samples.

This mainly attributes to the fact that the number of RHA particles per unit area was higher than the previous counterparts. Thus, trapped free water within the RHA particles and binder results in creating zones of unhydrated $CaSO_4$.

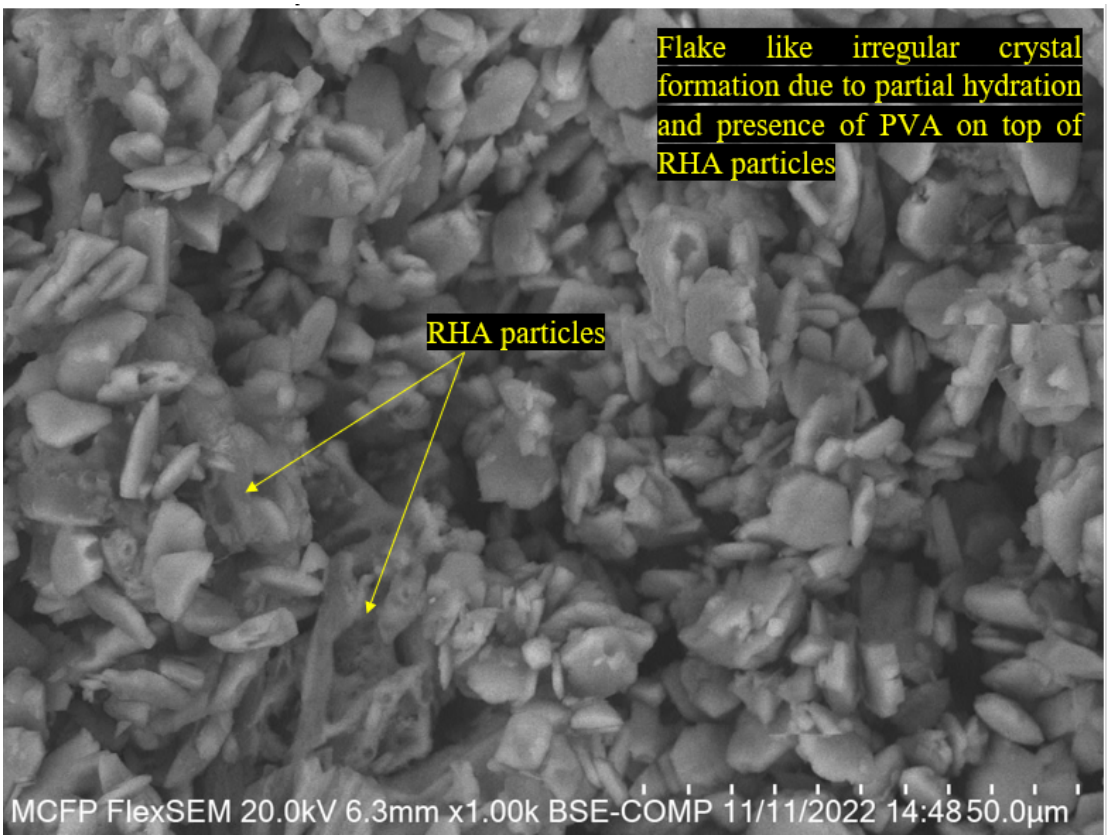

Figure 30: RHA particles and the crystal formation due to partial hydration and presence of PVA at x1000

On closer examination similar behavior and microstructure to 5% RHA was observed here. However, pores per unit area were slightly larger, with pore diameters greater than 100µm. Micropore presence was higher than 5% RHA but lesser than the control specimen. But whether this was constant throughout the entire sample was unclear.

-Microstructure of 10% RHA modified bandages

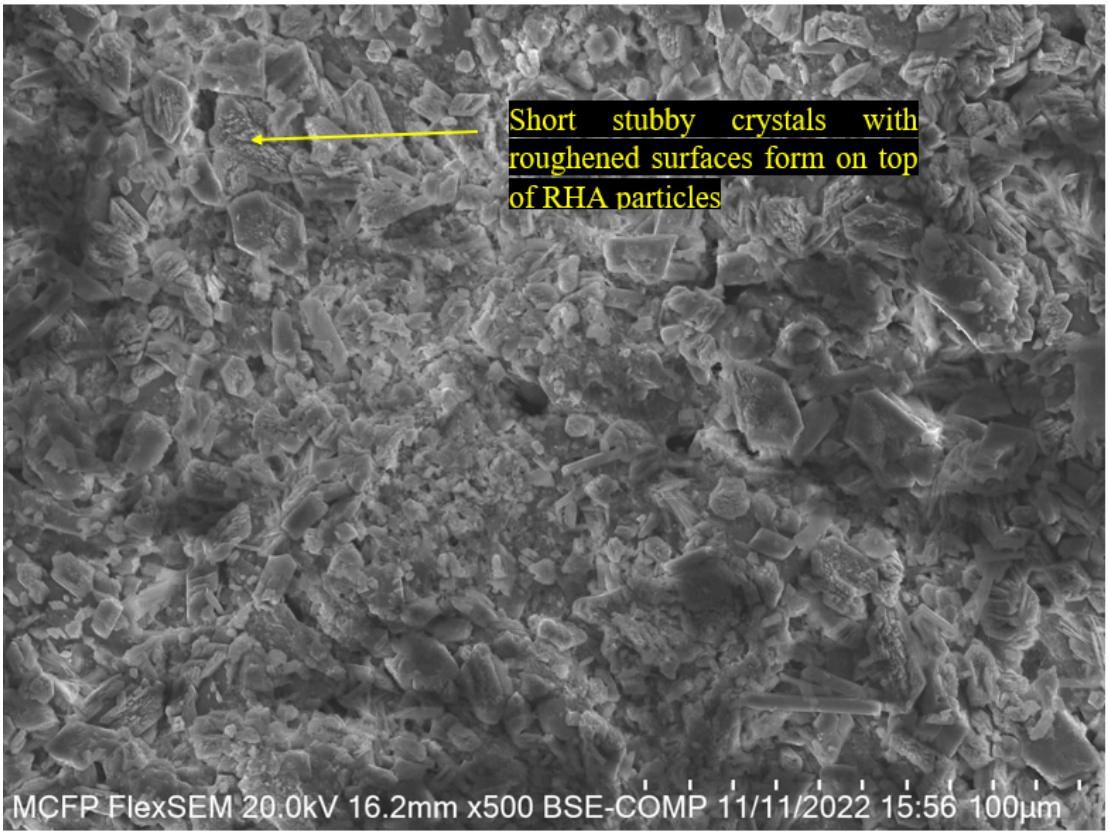

Figure 31: Crystal formation in 10% RHA modified bandages at x500

The 10% RHA modified bandages provided a lesser seen observation compared to other samples. A granulated appearance was seen on the $CaSO_4$ crystals. Badens et al. [110], state this was due to crystallization in the presence of a retarder. The PCE based superplasticizer, contains glucose as a retarder. Thus, the action of glucose within the batch water can be observed here.

15% RHA modified plaster samples

-Microstructure of the paste

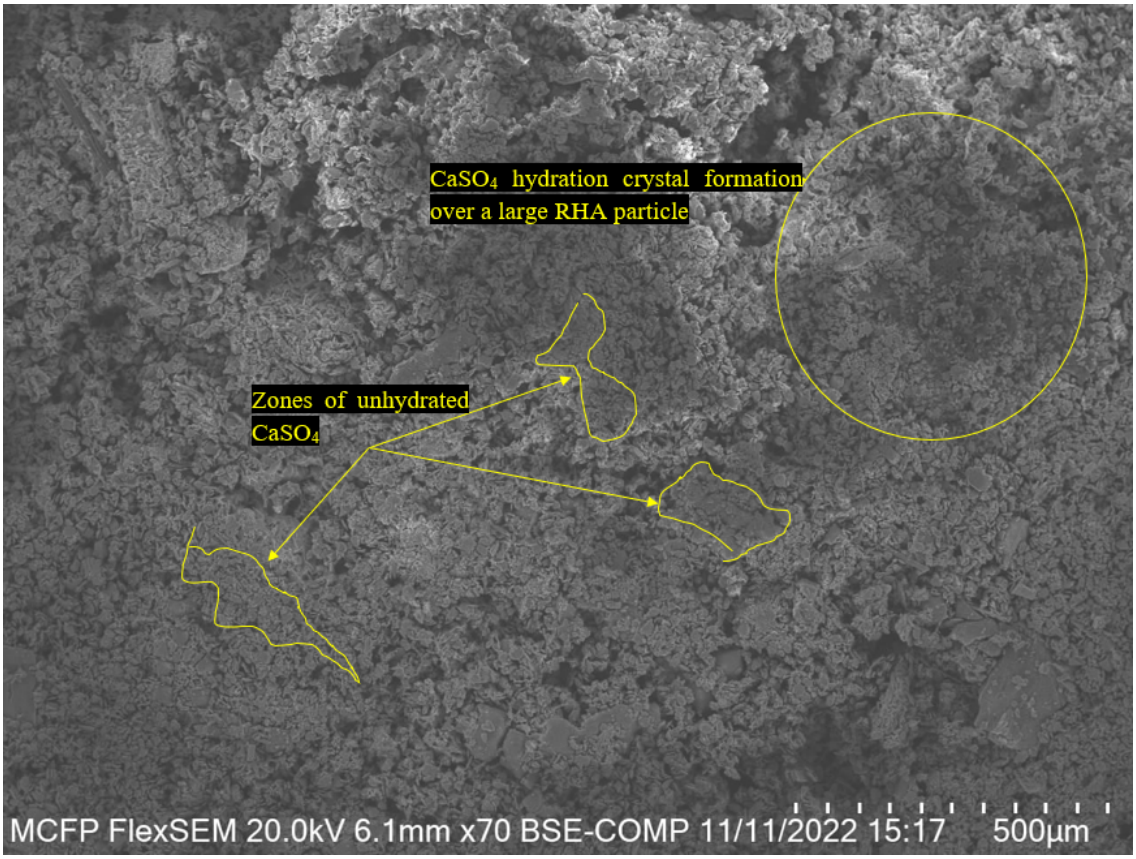

Figure 32: Microstructure of 15% RHA modified paste of the blend, showing unhydrated $CaSO_4$ zones x70

SEM analysis of 15% RHA samples recorded similar observations to the previous RHA samples in crystal formation and cracking.

However, compared to both 5% and 10% samples, a larger number of unhydrated zones were available. $CaSO_4$ hydration occurred on top of RHA particles in 15% RHA samples as well. Although there was abundant availability of pores, the microstructure was much

denser due to the presence of a large number of RHA particles per unit area and majority of the crystals forming on top of RHA particles due to the free water availability.

Figure 33: Crystal formation in 15% RHA modified samples x1000

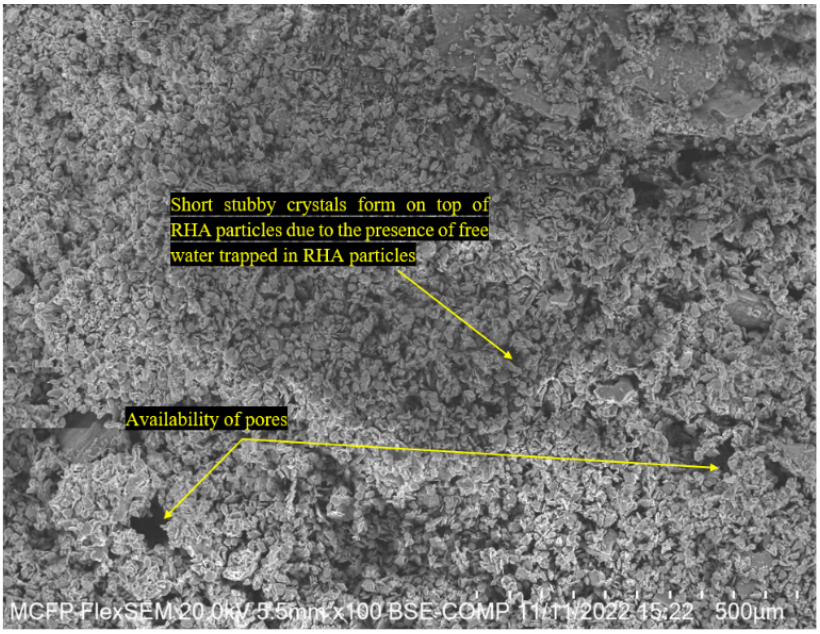

Figure 34: Crystal formation due to availability of RHA particles and presence of pores in the microstructure at x100

The nature of the crystals provided clear evidence that micro porosity was highly reduced. However, to gain a wholistic understanding the 15% RHA modified bandages were crucial.

-Microstructure of the 15% RHA modified bandages

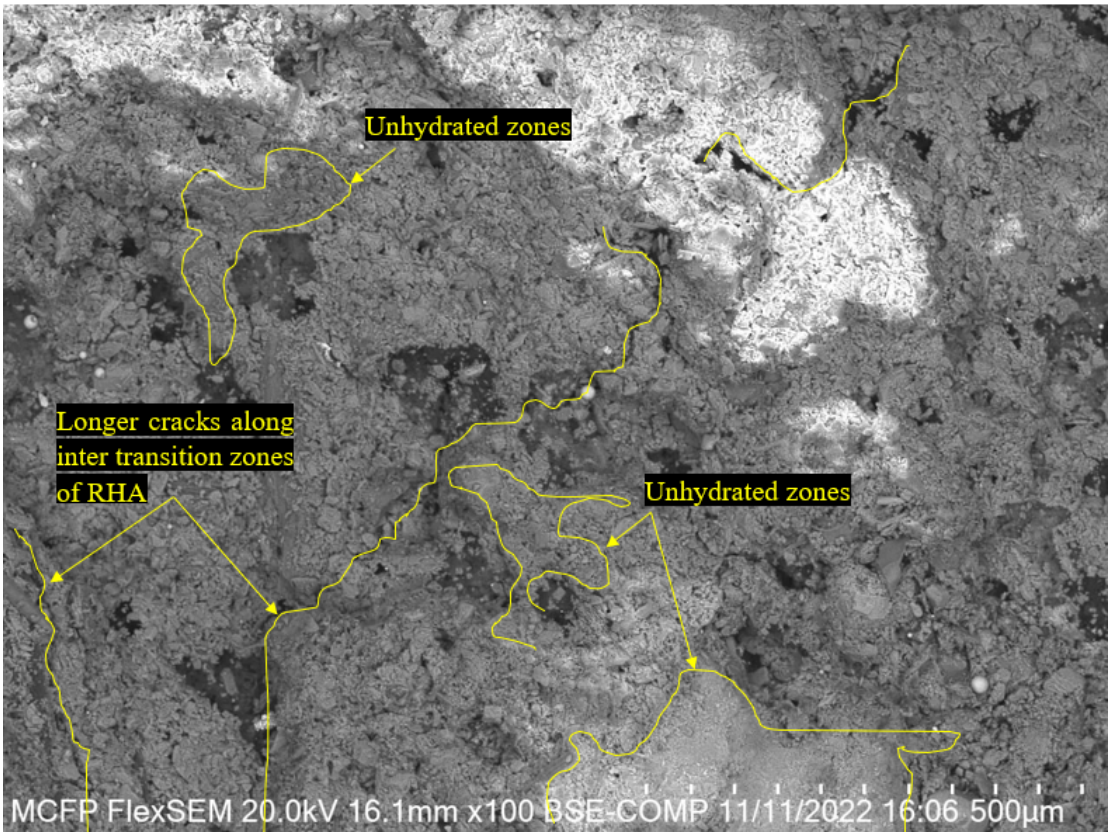

Figure 35: Microstructure of 15% RHA modified bandage samples with unhydrated zones and longer cracks, cracking increases with higher RHA percentages at x100

A larger availability of unhydrated zones and longer crack lengths were observed. Cracking was mostly localized around the inter-transition zones at the boundaries of RHA particles. However, plaster bandages provided clear evidence that majority of the

crystallization occurred on top of RHA particles at 7 days and areas around RHA boundaries were much weaker due to cracking.

Magnifications of x1000 show that microcracks were highly diminished in the sample but no methodical crystallization has taken place.

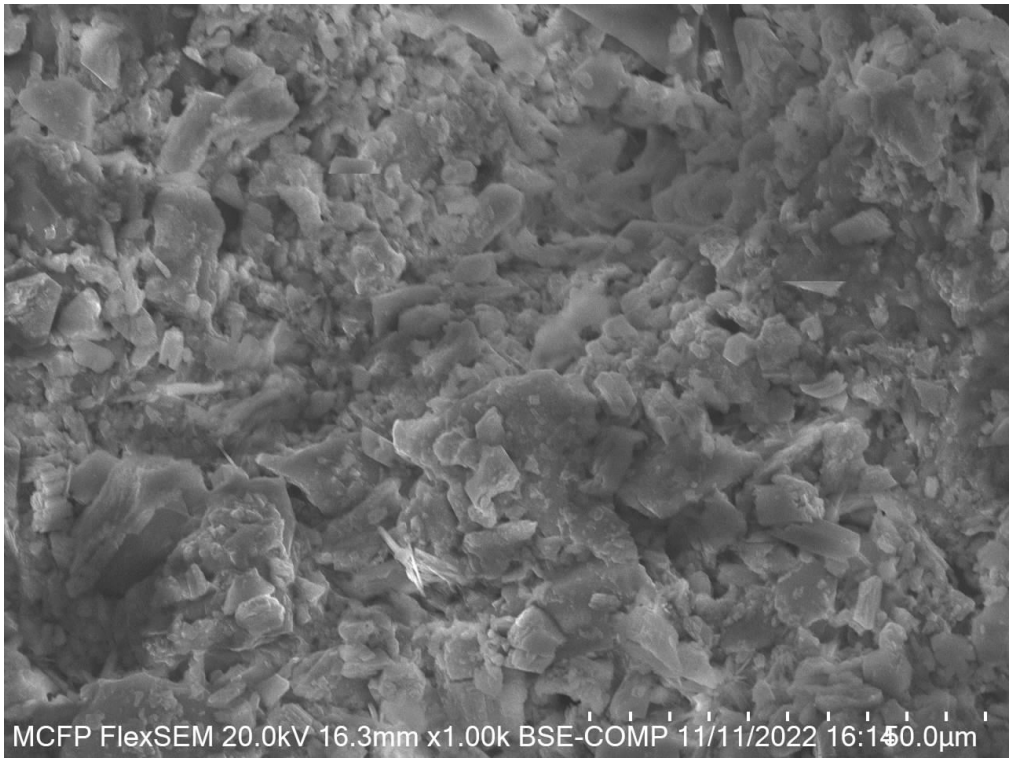

Figure 36: As RHA percentage rises microcracks have reduced but crystals are unmethodical and irregular at x1000

Discussion

The crystal formation occurs on top of RHA particles due to RHA entrapped free water presence. Thus, engulfing RHA particles.

Control samples show proper $CaSO_4$ crystal formation and presence of syngenite cores. However, different crystal formations are seen with the addition of RHA to the mix. The

short stubby flake like crystal formation and retarder and binder action on crystals are seen in the images. These variations of crystal formation lead to microcracking and crack localization around RHA particles. The microstructure observed here results in alterations in mechanical and thermal performance of the resultant composite.

5.6.2. Investigation of material porosity and breathability

Introduction:

The BET (Brunauer-Emmett-Teller) analysis holds significant importance in the characterization of plaster of Paris (POP) and its blends, due to its ability to provide valuable insights into the material's surface area and porosity. Here, Nitrogen adsorbate gas is exposed to the sample, gas molecules adhere to the material surface, covering both external and internal surfaces, including pores and cracks.

BET analysis allows for a precise measurement of the specific surface area, aiding in understanding the extent of hydration and the overall porosity of the plaster. This information is critical for optimizing the casting process, ensuring proper setting times, and enhancing the material's mechanical performance.

In this study the BET analysis was carried out to understand the porosity levels and surface area of the control and RHA modified plaster blends to gain an understanding on composition and formulation of the blends. These relate to the breathability, strength and comfort of the resulting cast. In the realm of medical applications, BET analysis becomes a valuable tool for quality control and process optimization, contributing to the development of plaster-based casts that meet stringent standards for patient care and recovery.

Sample preparation and Test Method:

20g of each sample category were obtained in finely grounded form to increase the surface area and allow for uniform gas adsorption. The samples were placed in an ampoule for degasification, to remove any adsorbed gases or volatile compounds that might be present on the surface.

Next, the degassed samples were accurately weighed and loaded into the Quantachrome NOVA 2200E BET for analysis.

Results and Analysis:

All nitrogen adsorption isotherms of hydration products of α and β $CaSO_4$ were of type II in the IUPAC classification with moderately high values of the C constant except for the 15% RHA modified sample. BET surface area (SBET) values between 30.685 and 7.631 m^2/g were obtained for the isotherms of the control to 15% RHA at an outgas temperature of 350°C. The desorption branches reveal a narrow hysteresis loop of H3 was evident in all RHA plaster blend samples with a slight variation in the control. However, all samples showed a narrow hysteresis loop of H3 type.

The BET surface area for each sample is tabulated below;

Table 16: BET surface and pore radius of tested blends

Sample category	BET surface area (m^2/g)	Pore radius (Å)
Control	30.685	17.193
5% RHA modified	26.007	17.1835
10% RHA modified	24.281	25.986
15% RHA modified	7.631	85.012

The S_{BET} reduced as the RHA content increased, with 15% RHA having the lowest BET surface area. A 75.1% reduction was seen in the 15% RHA compared to the control. 5% RHA blend recorded a 15.3% reduction of the S_{BET}. As S_{BET} reduces the effective particle size increases. This could be due to the blends having higher RHA content and the RHA particles contributing to the effective particle size of the blends. Thus, 5% RHA blends show a similar effective particle size to that of the control.

The pore radius obtained for samples, through the BJH method shows that micropore radius increases as the RHA percentage increases. SEM analysis showed that the size of the pores has increased. However, the availability of micropores diminished as the micropore volume decreased from 0.009 cc/g in the control to 0.004cc/g in 15% RHA samples. This is not a huge variation in pore volume. However, in relation to pore radius, as the RHA percentage increased the pores have moved from micropores to macropores.

Discussion:

BET analysis carried out here shows that as RHA % increases the micropores have been replaced by macropores that can be detrimental for the mechanical performance of the resultant plaster. Micropores are left behind when water evaporates at plaster hardening stage. This higher micropore radius can also be attributed to cracks localization around RHA particles and higher crack widths. This can grossly relate to improved cast breathability but their inhomogeneous distribution can greatly affect the S_{BET}. A S_{BET} has reduced with the RHA percentage, it proves that pores are not homogenously distributed throughout the sample.

The BET analysis was carried out for powders of the mix; thus, it can only provide a gross overview of the porosity and surface area of the blends, compared to mercury porosimetry which was not carried out for this study.

5.5. Mechanical Performance Analysis

5.5.1 Investigation on material weight and density

Introduction:

Developing a light weight plaster composite to reduce the bulkiness of the resulting plaster cast was one of the key objectives of this study. The material weight provides an understanding of how much the final cast weights and the weight reduction that can be obtained due to replacement of POP using RHA. According to Ezugwu at al., [111] addition of RHA into plaster panels resulted in an overall weight reduction of 15%. Studies show that RHA is a light weight material, that results in an overall weight reduction of the final composite.

Lightweight casts make it easy for individuals to carry out their daily activities while maintaining the required degree of immobilization for fracture healing. The reduction of excessive pressure on the skin, especially at joints and bony contours of the body reduces the tendency to develop pressure sores, skin irritation, bruising and blisters. This is critical in pediatric and elderly care.

Sample preparation and Test Method:

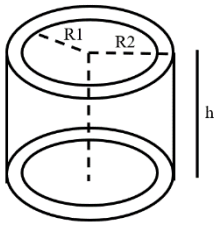

Figure 37: Dimensions of cylindrical samples developed according to ASTM C39

Hollow cylinders were made by;

Dipping the prepared plaster bandages in tepid water at room temperature (30℃- 35℃) for 1 minute until the plaster is creamy

and glistening. Then they were left to drain for 10 seconds onto another container before slightly compressing out the excess water.

Tight squeezing would force out water required for hydration and longer dipping times would exceed the critical point of plaster, causing degraded mechanical strength. This can result in material loss, which should be minimized in sample preparation.

The wetted bandages were layered up to 5 layers, R_2-R_1=15mm, cylinder height; h= 70mm. Generally, much larger samples are prepared according to literature, however, these sizes were selected to suite the minimal criteria specified by testing equipment used.

Each specimen was wrapped around a hollow tube of external diameter 25mm and left to set without any disturbance.

After about 3 hours, when the plaster bandages have lost the creaming glistening outlook, the tubes were removed and the plaster cylinders were allowed to dry at room temperature.

Sample preparation was done incompliance to ASTM C39 standard for compressive strength testing.

Figure 38: Cylindrical samples made of developed bandage samples for compression testing

The samples were left to set at room temperature for 7 days, before weighing. The weight of the prepared samples was measured using an electronic scale.

Results and Analysis:

- *Weight distribution*

Figure 39 shows the weight distribution of the samples tested for 7-day compression testing. This pattern was closely continued for all samples tested during the study.

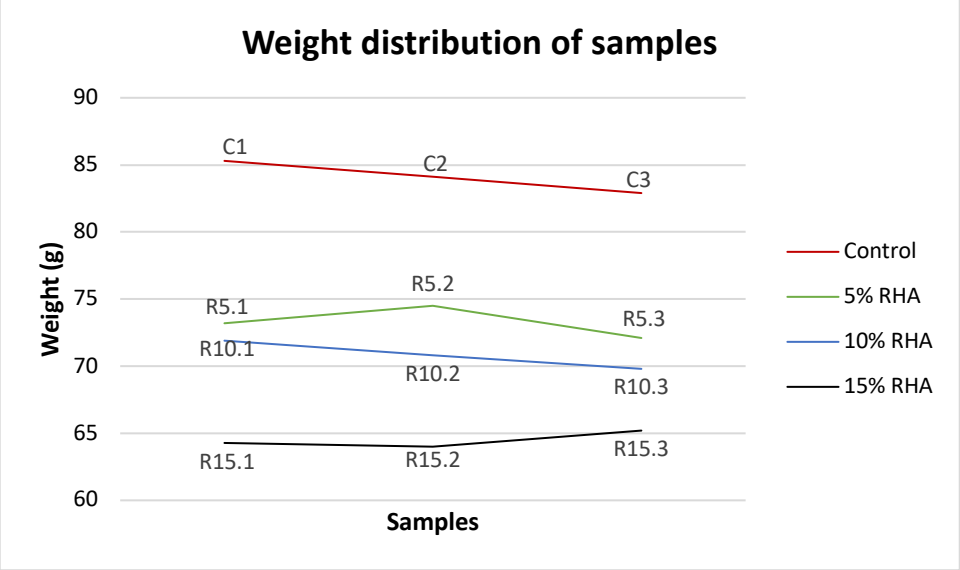

Figure 39: Weight distribution of cylindrical samples

The graphical representation of the weight distribution shows a gradual reduction in overall weight of the hollow cylinders casted out the RHA modified composite.

In comparison to the average weight of the control, 15% RHA modified cylinders show a 23% reduction in overall weight, while 12.9% and 15.8% weight reductions are observed in 5% RHA and 10% RHA cylinders, respectively.

Thus, higher replacements of RHA leads to reduction of the overall weight of composite.

- *Density*

According to Nduka et al. [112], RHA based material are less dense, due to the reduced weight of the resulting composite.

Gross calculation of density ($_{\varrho}$) is defined as the mass per unit volume of a material;

$$\boldsymbol{Density}\ (_{\varrho}) = \frac{\boldsymbol{Weight}\ (\boldsymbol{m})}{\boldsymbol{Volume}\ (\boldsymbol{V})}$$

When the resulting material is a composite each material density has to be calculated as a function of its mass.

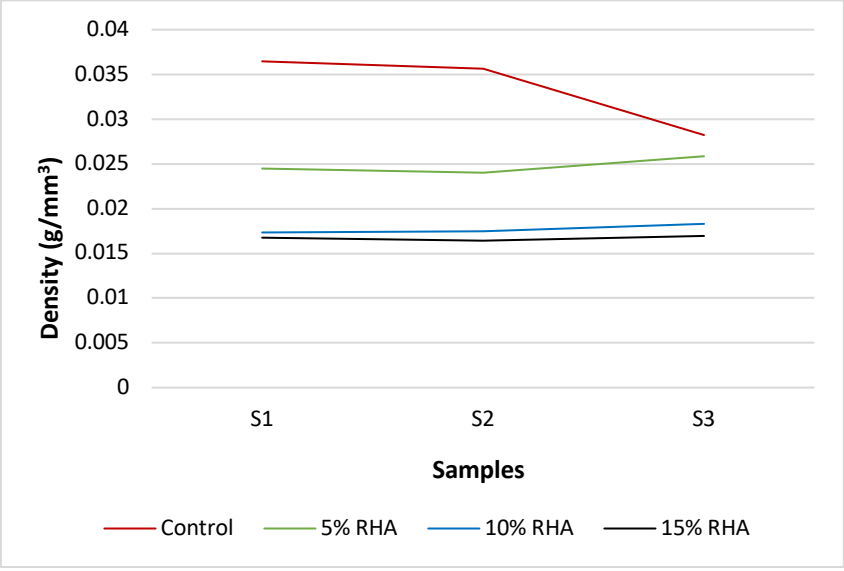

Figure 40: Density variation of tested samples -control and RHA modified samples

However, for this study a crude value for density is obtained to gain an overall understanding of density variation with variation of RHA percentage.

A higher density reduction is seen between the control and 5% RHA modified samples, while 10% RHA and 15% RHA samples do not show drastic reductions of density. This is mainly due to the reduction in weight with the RHA additions.

Discussion:

Microstructure of the RHA blends show that, as the RHA percentage increases, the amount of plaster per unit volume reduces. The RHA particles are macro particles, while the hydration crystals range from 10-50μms. Hence, a large area is occupied by RHA particles, compared to the syngenite and $CaSO_4$ crystals.

RHA is a light weight material and the higher presence of RHA per unit volume coupled with reduced volume of plaster per unit volume, reduces the overall weight of the composite. The S_{BET} reduces as the RHA percentage rises the void sizes increase. Thus, larger voids within the microstructure also contributes to weight reduction and thereby the reduced density of samples. Better homogeneity was found in the control than the RHA blends. Thus, higher packing density within the control, which translates to higher density of the control compared to the RHA blends.

5.5.2 Investigation of setting time - Vicat test

Introduction:

The most common drawback of plaster casts is their lengthy setting times in comparison to synthetic casts. To evaluate orthopedic plaster setting time, the Vicat apparatus was

used. It provides a quantitative measure of the time taken for the plaster to reach its maximum hardness and strength, which is critical for ensuring proper immobilization of a fractured bone or injured limb, as plaster is vulnerable during hardening. Orthopedic plaster, if disturbed on reaching the critical point and after, it loses its mechanical integrity permanently. Setting time also determines the time frame during which the plaster can be molded and shaped for better conformity.

Quantitative measurement of the plaster setting time helps to ensure consistency in manufacturing and quality control of orthopedic plaster products. Through the use of a standardized method for setting time determination, manufacturers can ensure that their products meet established quality standards and can perform reliably in clinical applications.

Sample preparation and Test Method:

Setting time was determined in accordance to the ASTM C191-19 standard test methods, modified to suite plaster.

The steps followed were:

1. Specimens were prepared, as 50mm x 50mm squares cut off from the plaster and dipped in tepid water (35℃). The soaked bandages were drained and lightly compressed to remove any excess water. Aggressive squeezing was avoided to reduce plaster flake off from the fabric. Generally, 67:100 is the commercially approved water to plaster ratio for orthopaedic plaster and this was maintained in the preparation of the plater bandages as well as in water immersion activation.

2. Activated plaster was layered on top of each other, until a 5-layer thickness was reached, (approximately 10 mm). A spatula was used to smooth the plaster surfaces and ensure proper adhesion among layers.
3. The Vicat apparatus was set up to observe the initial setting time using a 113.4 g weight and 1mm diameter needle attached to the plunger, as illustrated under Figure 41.

Figure 41: Vicat apparatus set up for initial and final setting time measurement of the tested samples

4. The needle was allowed to penetrate the surface of the plaster every 30 seconds until the plaster starts to lose its creamy consistency, lose its surface luster and appear grainy; i.e when it passes the critical point.
5. Generally, initial setting time was recorded when the needle could only penetrate half the plaster thickness (i.e., 5mm), but as we are working with plaster coated fabric this was when the plaster has attained the consistency of a thick cream.

6. The test was repeated every 30 seconds after the initial setting time was recorded, with until the needle could no longer make any visible indentation on the surface of the plaster or the plaster appears grainy. This was the final setting time.
7. A stopwatch was used to record timing.

Results and Analysis:

The setting time of orthopedic plaster can vary depending on factors such as the mixing ratio, material composition and temperature and humidity of the environment. Temperature, humidity and air circulation affects the rate of water evaporation which directly affects the rate of hardening, hence the setting time.

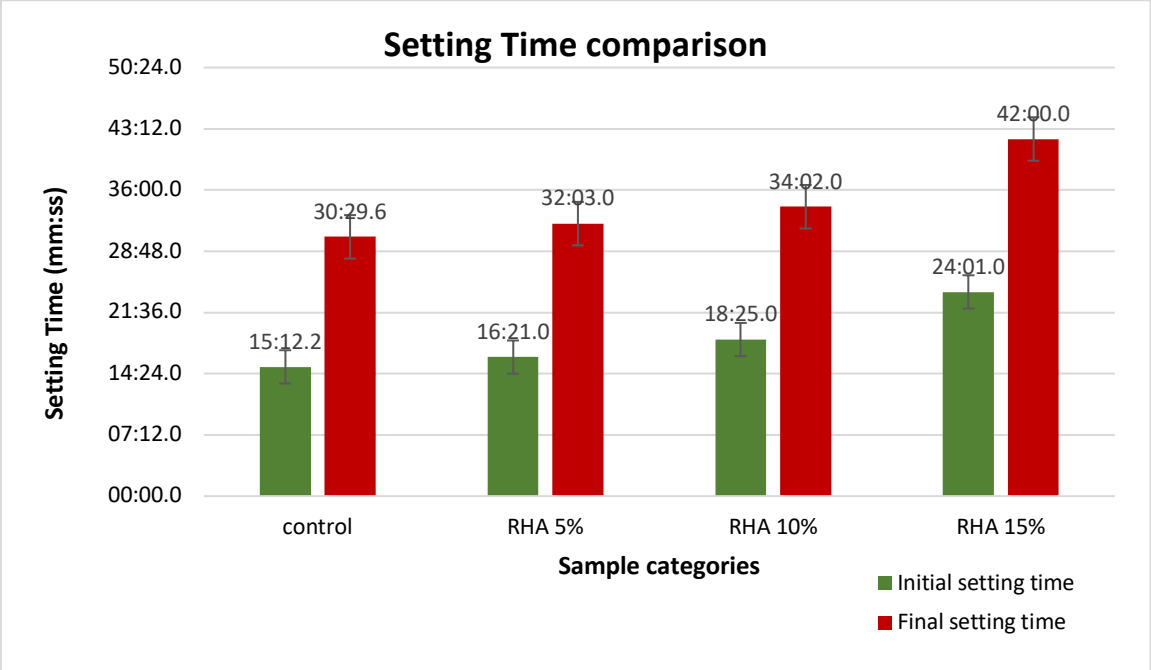

Figure 42: Setting time comparison of tested samples

The tests carried here were done at room temperature of 24-25℃ and relative humidity of 87-92%. The averaged setting times taken for each sample category are shown in Figure 42.

The vicat test shows that the setting times of the RHA samples steadily increased with increasing RHA content. Both initial and final setting times increased compared to the control mix.

The control mix shows a initial setting time of 15:12 minutes while the final setting time was 30:30 minutes. 5% RHA modified samples closely mimic the initial and final setting times of the control, with only a 7-5% increase. 10% RHA modified samples record a 12.3-20% increase in setting time than the control. However, 15% RHA modified samples record a 38.6 % increase in setting time compared to the control.

Discussion:

Microstructure analysis shows at the presence of K_2SO_4, acts an accelerator, causing POP to rapidly hydrate. Moreover, the control undergoes hardening and volume expansion, as water is readily available for hydration. The formation of syngenite accelerates the setting of gypsum due to two factors: First, syngenite forms rapidly in large cores and, second, the presence of such large cores speeds the formation of dihydrate crystals.

Studies show that uncontrolled burnt RHA are hygroscopic in nature [113] and attracts free water available for hydration. Therefore, higher RHA percentages lead to longer setting time, as free water is trapped by the RHA particles. Plaster hydration requires the formation of $CaSO_4.2H_2O$ which cannot effectively occur when water is scarce.

Percentages of 15% RHA entraps more free water than other RHA blends due to higher RHA percentage per unit volume of samples. Leading to prolonged setting times.

The setting time testes were carried out for the bandage specimens. The underlying cotton bandages too retain a significant amount of water when wetted for layup, then the paste of the blends. Thus, the setting times of the bandages are elevated than the set times for pure blends. The bandage samples were used to gain a more realistic understanding of the setting time increment of the end product.

Further retardation of the setting time was supported by the presence of glucose as a retarder in the superplasticizer. Thus, it is crucial to search for the optimal retarder percentage for the superplasticizer mixes to allow ample time for initial plaster preparation but will not prolong the setting times of the final product.

5.5.3 Investigation of water absorption- Bead test

Introduction:

Plaster of Paris casts are highly vulnerable to water. Upon water exposure the casts lose their mechanical strength characteristics and often tend off to break as $CaSO_4$ rehydrates forming $CaSO_4.2H_2O$.

This makes it tedious for patients fitted to POP casts to interact with water, during day to day activities such as bathing, making activities such as swimming is impossible. Therefore, there is a very high demand for the use of synthetic casts which show high resistance to water penetration.

RHA is known to improve resistance to water penetration in cementitious composites. Studies show superhydrophobic coatings fabricated from treated RHA. RHA comprise of 97.5 wt.% SiO_2, which is known for their near superhydrophobic properties [114, 115]. The combination of RHA and superplasticizer is able to modify the concrete structure, improving the water resistance up to 50% due to compaction of the structure.

This study uses the water droplet test to crudely understand the water repellency of the prepared samples and compare the results with the control. The water droplet test is a simple and quick method used to assess the water repellency of a fabric /material.

The following steps were carried out to quantify the water repellency of the test specimens based on the time it took to completely absorb an applied water droplet.

Sample preparation:

The bandage sample was cut off from the prepared bandages. 5 layers of 50mm x 50mm bandages were applied on top of each other and were left to dry at room temperature (22± 2°C) for 7 days. 3 samples were prepared from each category, to calculate the average value. This allows us to gain a normalized value for each sample category. The samples should be placed on a flat surface exposed to the atmosphere. This layup mimics the normal manner in which plaster casts are after being applied to patients.

After the samples have adequately dried at room temperature for 7 days, the water droplet application is carried out.

Test Method:

A droplet of water is applied to the surface of the fabric using a pipette/ dropper. The size of the droplet and the height of the dropper can affect the results of the test, so it is important to use consistent application techniques. Hence, a standard pipette was used to apply the water droplets.

The droplet is allowed to sit on the plaster surface until it completely disappeared from the surface. Time taken was calculated using a stop watch. Each sample from each category was tested four times to eliminate any surface irregularities that might affect the bead time.

During this time, the behavior of the droplet was observed. If the droplet beads up and rolls off the fabric surface, the plaster is considered water repellent. If the droplet is absorbed into the plaster or spreads out over the surface, the fabric is considered water-absorbent.

However, the water droplet test is a quick and simple method for assessing the water repellency of fabrics, but it is not as precise or standardized as other testing methods such as ASTM D6904. It is often used as a preliminary screening test before more rigorous testing methods are employed. As the bead test was carried out as a preliminary screening no such rating system was necessary. Only a comparative analysis was carried out.

Results and Analysis:

The timing obtained for each sample are tabulated below;

The sample code is denoted as per;

S1-1; where S1 refers to sample 1 of each category and the number after the hyphen is the respective test attempt

Table 17: Average bead time calculation for each tested sample

Time (sec)				
Sample Code	**Control**	**RHA Samples**		
		5%	**10%**	**15%**
S1-1	00:00.7	00:22.0	00:18.0	00:15.0
S1-2	00:01.9	00:28.1	00:24.0	00:18.8
S1-3	00:00.8	00:16.3	00:14.2	00:10.3
S1-4	00:00.6	00:49.8	00:10.3	00:09.4
S2-1	00:00.6	00:24.0	00:18.0	00:40.2
S2-2	00:01.3	00:40.1	00:28.5	00:14.7
S2-3	00:01.0	00:28.9	00:31.2	00:49.3
S2-4	00:00.5	00:01.0	00:15.4	00:28.0
S3-1	00:00.6	00:16.9	00:34.0	00:49.4
S3-2	00:04.6	00:28.5	00:32.0	00:08.9
S3-3	00:01.8	00:12.7	00:24.2	00:14.0
S3-4	00:01.4	01:00.7	00:30.1	00:23.3
Average Bead Time (sec)	00:01.2	00:25.3	00:21.5	00:21.6

None of the water beads rolled off, proving that the samples are not water repellent. However more beading was seen all RHA modified samples compared to the control, where no beading was observed. All RHA modified samples show an increase in the time for the bead to be absorbed.

It is evident from the test results obtained that RHA samples are comparatively water repellent than the control. However, the above graph shows each sample and test cycle's bead time variation.

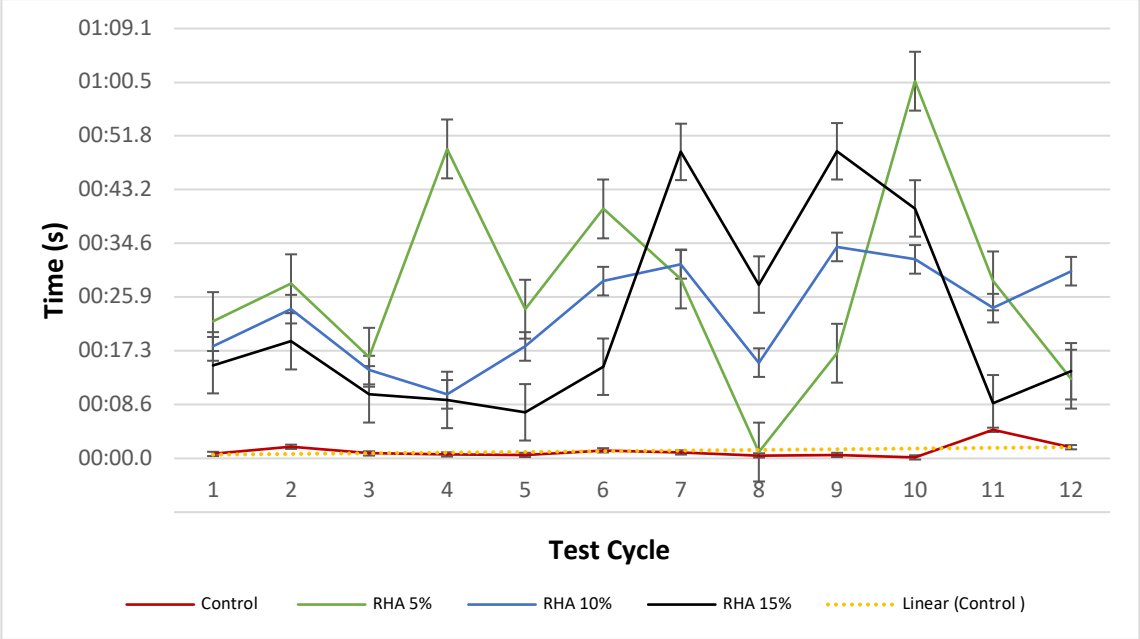

Figure 43: Bead time alteration of different samples per test cycle

According to Figure 43, it is evident that a relatively high bead time is observed in samples with 5% RHA replacement. All the values obtained for bead absorption was less than a minute. Practically, these are much lower values and would not account for water repellency in casts. However, it can be seen that addition of RHA does improve the water repellency of highly water susceptible plaster casts.

Discussion:

The microporosity and higher amount of plaster per unit volume, makes the control samples highly susceptible to degradation due to water. Thus, water bead tends to get

absorbed quickly undergoing rehydration of $CaSO_4$. This tendency is reduced in the RHA blends with 5% RHA blends showing better waterproofing than the other two categories. This property is mainly attributed to the fact that the 10% and 15% RHA blends have more unhydrated zones compared to the 5% RHA blend. When water droplets come in contact with the plaster unhydrated zones quickly absorb the water undergoing hydration.

However, compared to the control, the RHA blends have unburnt RH particles that have a thick water-resistant outer covering which repels water beads to a certain extent in the mix. Closer observations into the microstructure shows majority of the plaster crystallization occur on top the RHA particles in 10% and 15% RHA blends. Compared to the 5% RHA blend, the $CaSO_4$ crystals formed on top of the RHA particles get exposed to the water bead undergoing rehydration. Thus, absorbs the water bead.

In comparison to the synthetic immobilization material and water-resistant fabric, all samples are poor performers in water resistance.

5.5.4 Investigation of compressive strength

Introduction:

The compression strength test is a standard method used to determine the load-bearing capability or compressive strength of materials. This ensures that the plaster used in these casts can withstand the weight and forces acting on the limb without breaking or losing its mechanical integrity. A cast with insufficient compressive strength could lead to potential complications, reinjury and discomfort for the wearer.

Further, this test is used as a basic quality assurance in medical applications to meet required quality standards. Different patients may require casts of varying strength depending on factors such as the nature and location of the injury, patient weight, or activity levels. The compression strength test aids healthcare professionals in making informed decisions about the most suitable plaster material for individual patients.

Literature generally carries out 24 hours to 7-day compressive strength analysis. It is not sufficient to assume a cast will reach full strength within 24 hours after application, especially for plaster-based casts. In wet and humid climates, the drying and strength gain is prolonged from 36 hours to a number of days [26].

However, this study analyses the 14 days compressive load bearing ability as most casts were fitted to patients for over a period of 4-6 weeks where, the compressive strength of the cast material is crucial during the first 2 weeks, to promote proper alignment of the fracture. This is the time over which inflammation control, tissue repair initiation, scar tissue formation, hematoma organization, proper bone alignment and protection from reinjury is carried out. Thus, the cast material has to provide robust mechanical strength properties like compression and tensile strength.

In this study, the modified plaster casts are necessarily subjected to compressive strength testing even under the preliminary investigation, to eliminate any material combinations that did not meet the threshold value (*the control sample provided the threshold*). The compression tests were carried according to the ASTM C39 standards.

Sample preparation and Test Method:

Cylindrical samples were used as they adequately model a typical fracture cast. Compression testing was carried out confirming to ASTM C39 standards, with slight modifications to suite the Instron 5569A Mechanical Tester with a 5kN to 50kN load cell. The samples were layered up to a 5-layer thickness of 15mm and a height of 70mm. The cylinders were trimmed to gain the desired dimensions to be fitted to the mechanical tester and smoothened to assure uniform compression.

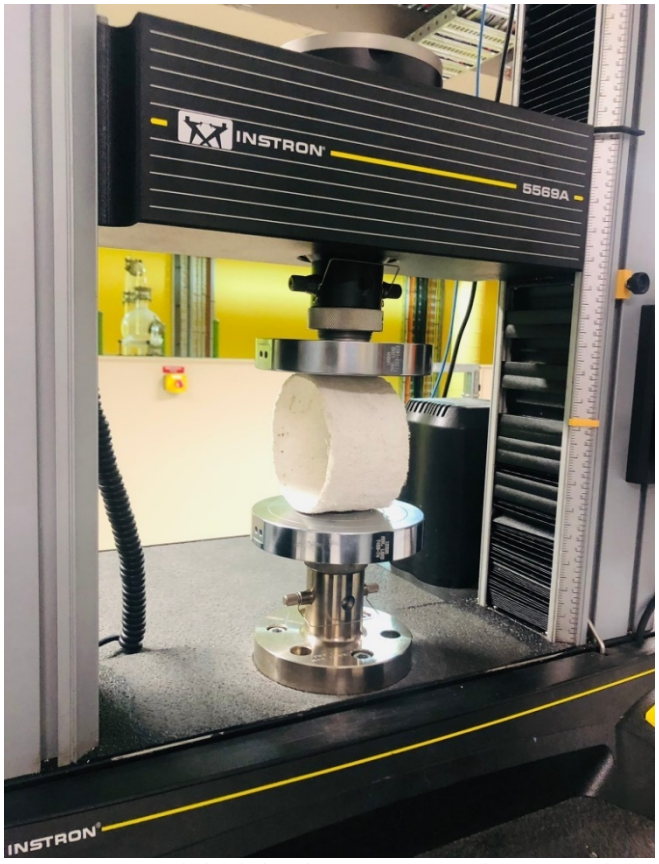

Figure 44: Sample loaded to the Instron 5569A for compression testing

The specimens were subjected to testing as shown under Figure 44. The load was slowly added at a rate of 150N and the compressive loads were recorded by the load cells every 0.1s. Samples were tested at intervals of 24hrs, 7 days and 14 days.

For cylindrical specimens as shown in Figure 38, the calculation of the compressive strength is as follows;

$$\textbf{Compressive Strength } (\sigma_C) = \frac{\textbf{Maximum Compressive Force(F)}}{\textbf{Cross} - \textbf{sectional Area } (A)}$$

During the compression strength test, the Instron records the maximum force applied to the sample just before it fails or fractures.

For cylindrical samples, the diameter (d) of the sample was measured using Vernier calipers. Then, calculated using the cross-sectional area (A) formula:

$$A = \pi\left[\left(\frac{d}{2}\right)\right]^2$$

The maximum compressive force (F) was divided by the cross-sectional area (A) to calculate the compressive strength (σ) of the material:

$$\sigma_C = {}^{F}/_{A}$$

However, on average all samples were maintained at the same cross-sectional area; the compressive strength was directly proportional to the maximum compressive load the samples underwent.

Results and Analysis:

The maximum compressive loads of each sample averaged are tabulated below;

Table 18: Average load to failure in 24 hours, 7-day and 14-day compression testing of samples

Time interval	Sample category	Sample code	Load to failure (kN)	Average Load to failure (kN)
24 hours	Control	C1/24	0.51	0.57
		C2/24	0.61	
		C3/24	0.59	
	5% RHA	RHA 5-1/24	0.7	1.14
		RHA 5-2/24	0.81	
		RHA 5-3/24	0.74	
	10% RHA	RHA 10-1/24	1.02	1.15
		RHA 10-2/24	1.5	
		RHA 10-3/24	0.98	
	15% RHA	RHA 15-1/24	1.08	1.4
		RHA 15-2/24	1.6	
		RHA 15-3/24	1.52	
7 day	Control	C1/7	0.3	0.2
		C2/7	0.25	
		C3/7	0.32	
	5% RHA	RHA 5-1/7	1.52	1.65
		RHA 5-2/7	1.7	
		RHA 5-3/7	1.73	
	10% RHA	RHA 10-1/7	1.64	1.4
		RHA 10-2/7	1.3	
		RHA 10-3/7	1.26	
	15% RHA	RHA 15-1/7	0.98	0.95
		RHA 15-2/7	1.0	
		RHA 15-3/7	0.87	
	Control	C1/14	0.42	0.306
		C2/14	0.31	
		C3/14	0.371	
	5% RHA	RHA 5-1/14	0.13	1.39

14 day		RHA 5-2/14	1.44	
		RHA 5-3/14	1.41	
	10% RHA	RHA 10-1/14	2.01	2.09
		RHA 10-2/14	1.98	
		RHA 10-3/14	2.28	
	15% RHA	RHA 15-1/14	1.56	1.5
		RHA 15-2/14	1.48	
		RHA 15-3/14	1.46	

- *24 Hour Compression Analysis*

At 24 hours the samples showed minimal strength gain with the control specimen showing the lowest compressive load bearing capability, while 15 % RHA modified samples showed the highest load bearing capacity at 1.4 kN, compared to the control, which was only 0.57kN.

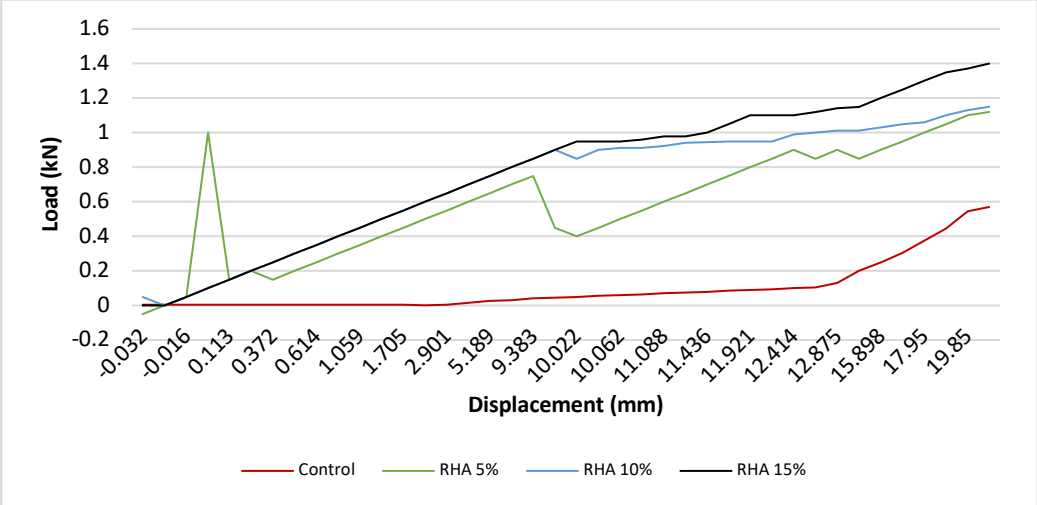

Figure 45: Variation of compression loading for tested samples at 24 hours

Depending on the relative humidity of the environment and the room temperature at which the samples were allowed to dry, the control samples showed faster drying compared to

the RHA modified samples as observed during the vicat test. However, all samples retained moisture and this clearly resulted in the low compressive load bearing abilities for all samples.

Compared to the control the RHA modified samples were wetter. During the compressive loading much of the retained water was forced out of the RHA modified samples and this resulted in compression values being significantly higher. The compressive strength values were partially due to the force expended to remove the entrapped free water from the RHA particles.

- *7 Day Compression Analysis*

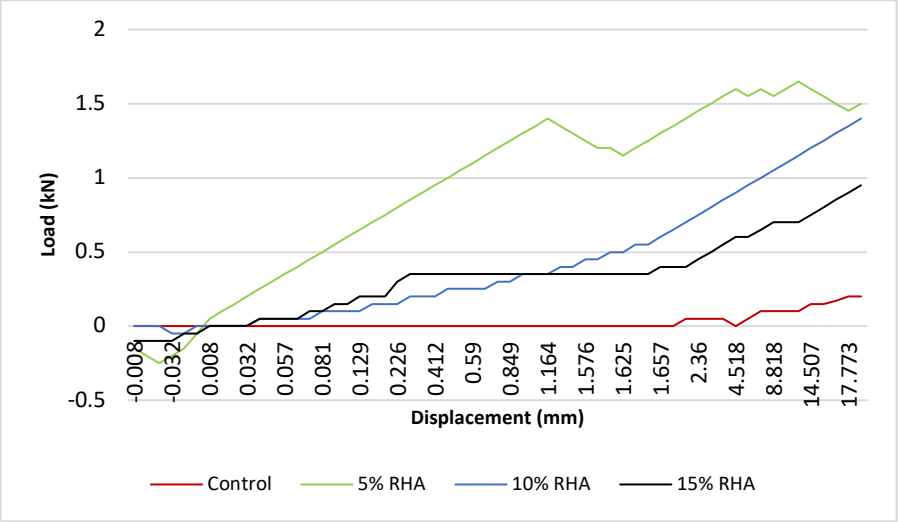

Figure 46: Variation of compression loading for tested samples at 7 days

At 7 days, all samples are fully dried at room temperature, with minimum moisture intact. The average compressive loads the samples could withstand were 0.2kN, 1.65 kN, 1.4 kN and 0.95 KN respectively. It is evident that the control sample recorded a 64% reduction

in the compressive load bearing ability. This was mainly due to the material flake off from the bandage and the delamination of the bandage layers.

The 5% RHA recorded ultimate loading at 1.65kN which was a 44.7% gain than the 1.14kN at 24h. However, comparative to all samples tested, 5% RHA samples showed maximum weight bearing capacity at 11mm displacement but failed after displacing an additional 6.2mm at a loading of 1.5kN. The shape of the compression loading curve observed was different from all other samples as they peaked and failed at maximum loading.

10% RHA modified samples recorded a strength gain of 21.7% at failure. However, the load bearing capability of 15% RHA specimens considerably reduced from 1.4kN at 24 h to 0.95kN at 7 days.

-14 Day Compression Analysis

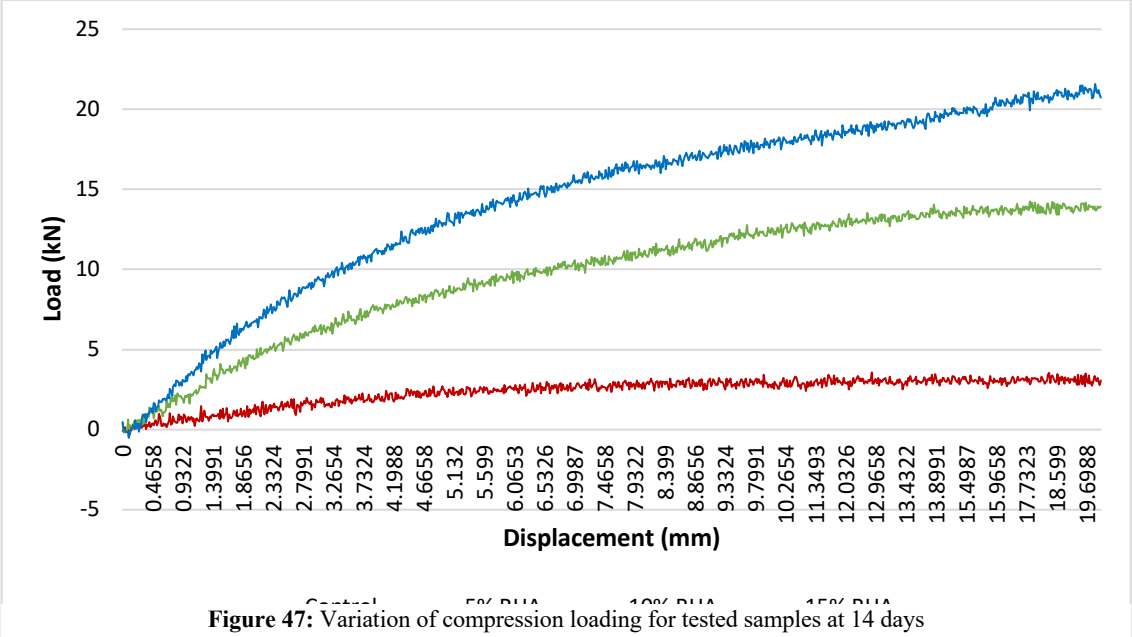

Figure 47: Variation of compression loading for tested samples at 14 days

At 14 days compression testing, the results show that the control and the 5% RHA, 10% RHA and 15% RHA modified specimens record 0.306kN, 1.39 kN, 2.09 kN and 1.5 kN, respectively. Control samples recorded a loss of compressive load bearing ability at 7 days but have regained 53% at 14 days. This is due to all the moisture coming to the surface and evaporating leaving a dense structure of α and β $CaSO_4$ crystals that improves the strength of the structure. Further, material flake off had already diminished due to the unavailability of moisture, allowing the structure to properly set. The remaining material remains bound to the base plaster via binder action.

5% RHA modified samples recorded very high strength properties at 7 days compared the rest. At days, a 20.1% loss of compressive load bearing ability was recorded. 10% RHA samples which only recorded1.4 kN at 7 days, recorded a 49.2% strength gain at 14 days.

According to Figure 48, 10% RHA samples show consistent compressive strength gain while 15% RHA samples recorded a 32.1% loss at 7 days and a 57.9% gain at 14 days.

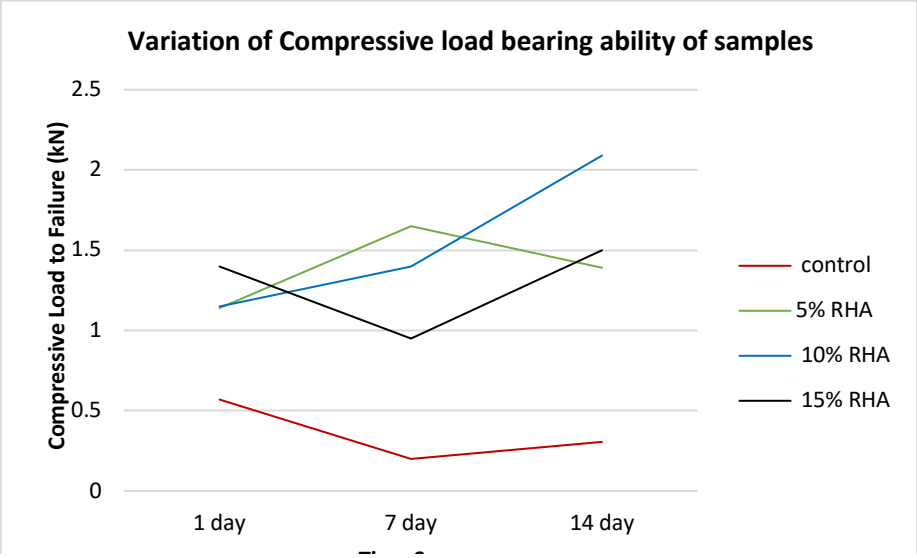

Figure 48: Comparison of the variation of compression loading for tested samples

Hence, in terms of compressive strength, 10% RHA replacement samples recorded a consistent compressive strength gain over the 14 -day period.

Discussion:

As the RHA percentage increases, RHA particles remain entrapped within the matrix. SEM images show crystals growth on top the RHA particles, due to free water entrapped by RHA in the mix.

In terms of mechanical performance, the microcrack accumulation and higher micropore density per unit area leads to reduction in mechanical strength of the control. The optimal strength gain for the control is at 24 hours due to majority of the plaster hydrating and contributing to the crystal formation. Thus, at 24 hours control samples undergo adequate hydration, with 0.57kN compression load bearing.

At 7-14 days plaster casts are required to show good compressive strength properties, to enable proper fracture alignment. Immobilization material such as traditional plaster easily loses their strength properties at 1.5-2 weeks, due to material flake off and degradation due to contact with body fluids, moisture and water. Hence, the testing for compressive load bearing at 7-14 days is imperative to the study.

The aforementioned was observed in the control, with much material flake off observed at 7 days as the samples undergo full drying. Water evaporates, leaving micropores that degrade strength. At 14-days a slight strength gain occurs due to the remaining plaster hardening with little to minimal unhydarted plaster available. This results in a more

homogenous microstructure. Wicking effect has already been established at 7 days and syngenite cores remain intact at 14 days.

The RHA modified blends show better mechanical performance compared to the control, as they possess a denser microstructure composed of larger, stubby crystals.

5% RHA modified samples possess less cracking at IT zones, a denser microstructure and a lower micropore density than other RHA counterparts. The pore radius remains slightly decreased than the control. 5% RHA samples comprise less unhydrated zones. This relates to its overall better performance at compression at 24 hours to 7 days.

At 24 hours all RHA samples retains moisture, thus majority of the load bearing is done by the RHA particles in the mix. Higher presence of RHA per unit volume relates to higher compressive loading. Thus, 15% RHA modified samples perform better at 24-hour compression tests. This cannot be crudely obtained as the early strength of the samples, due to inadequate drying.

All RHA modified samples undergo pozzolanic reactions with gypsum. This adds to the overall strength of the composite, which is mostly likely the underlying reason for the strength gain at 7 days. 5% RHA blends undergo full evacuation of entrapped free water within 7 days, reaching an optimal microstructure. This relates to optimal mechanical and thermal performance at 7 days. However, by 14 days minimal to no pozzolanic activity occur, especially within the 5%RHA blend. Thus, compressive strength reduces. The flake off of material from the base plaster, contributes to lower the compressive strength of the 5% RHA blends.

10% RHA samples comprise of crystal formation localized on top of the RHA particles, with lower microcrack and micropore density. As the samples do not undergo complete drying at 24h, water remains trapped within the matrix, due to RHA and binder water absorption. However, at 7 days when the samples are completely dried, However, some free water remains entrapped by RHA particles. SEM images of 7-day samples show slightly higher unhydrated zones localized around RHA particles, with crack widths and pore diameters larger in comparison to the 5% blends. Further, the high open burnt RHA content (containing minute particles of unburnt rice husk) loosens up from the underlying plaster bandage (the binder strength is not adequate to hold the large RHA content available) and the dry mix tends to flake off. This results in delamination between respective plaster layers and material loss. Collectively this results in a strength gain lesser than 5% RHA samples. Strength returns at 14 days when pozzolanic activity has peaked for 10% RHA samples. The RHA content in 10% samples creates a balanced microstructure, striking a volumetrically near balance in the core material quantities. This gives more homogeneity within the mix compared to 5% and 15% RHA samples. Although it ideally should record higher microcracks at inter-transition zones at 14 days, 10% RHA modified samples recorded very good compressive strength gain due to the entrapped free water contributing to the hydration of unhydrated plaster, creating a denser microstructure and lessening the number of capillary pores present. Thus, peaking in compressive strength.

15% RHA modified samples underwent high loading even at 24hrs, although samples remained moist. This was due to the abundance of RHA particles which bore most of the

loading. However, similar to the control, the 15% samples too showed strength reduction at 7 days due to material flake off which is mainly due to high RHA per unit volume. This causes low adhesion of the mix to the bandage. Larger voids and abundance of unhydrated zones too contribute to this. Strength gain occurs at 14 days similar to that of 10% RHA samples.

However, 10%RHA modified samples performed better in compression until 14 days, with 5% RHA modified samples closely following.

5.5.5 Investigation of wet crush strength

Introduction:

Wet crush strength is a crucial parameter for orthopedic plaster casts due to water's significant impact on the integrity and performance of these medical devices. Plaster casts generally come in contact with water and bodily fluids during long term immobilization and daily chores such as showering.

However, wet crush strength is crucial during the first few days of immobilization as the cast gains strength over time and is highly susceptible to water degradation and strength loss throughout its life cycle. Testing for wet crush strength was carried out with a slight modification, i.e. immersion in tepid water at 35°C. This was to ensure close mimicry of the body fluids and water such as hot showers.

Sample preparation and Test Method:

Samples were developed according to ASTM C39, following the same procedure for 7-day compression testing. (Refer 5.5.4).

The samples developed were immersed in tepid water at 35°C for 30 seconds and left to dry at room temperature for 5 minutes. The testing procedure was the compression testing discussed under 5.4.4.

Results and Analysis:

The average weight of the samples before and after water immersion and the wet crush compression loading results are tabulated below;

Table 19: Weight alteration before and after water immersion

Sample category	Average weight before water immersion (g)	Average weight after water immersion (g)
Control	84.1	98.23
5% RHA	73.26	76.42
10% RHA	70.83	75.67
15% RHA	64.5	72.68

Table 20: Wet crush strength results of tested samples

Time interval	Sample category	Sample code	Load at failure (kN)	Average Load at failure (kN)
24 hours	Control	C1-T	0.018	0.021
		C2-T	0.023	
		C3-T	0.022	
	5% RHA	RHA 5-1-T	0.131	0.129
		RHA 5-2-T	0.136	
		RHA 5-3-T	0.120	
	10% RHA	RHA 10-1-T	0.152	0.137
		RHA 10-2-T	0.129	
		RHA 10-3-T	0.130	
	15% RHA	RHA 15-1-T	0.074	0.076
		RHA 15-2-T	0.081	
		RHA 15-3-T	0.073	

Based on the results it is evident that the control samples performed poorly under wet crush compression compared to the RHA modified specimens.

The control sample records an average load at failure of 0.021kN which is 9.5 times lower than the compression load bearing ability at 7day compression.

All samples performed poorly at wet crush compression compared to their 7-day compression of dry samples. 10% and 5% RHA samples showed comparatively higher load bearing capabilities than the control, which were 0.137kN and 0.129kN, respectively. The 5% RHA modified specimens recorded 6.14 times higher wet crush compression performance than the control, while 10% RHA samples recorded an average of 6.52 times higher load bearing capabilities. 15% RHA replacement samples were only able to withstand 0.076kN compression loads on average. Thus, 15% RHA samples performed poorly at wet crush compression among all RHA modified samples. 10% RHA samples recorded the highest wet crush compression load bearing ability among all tested samples, which was 6.2% higher than 5% RHA.

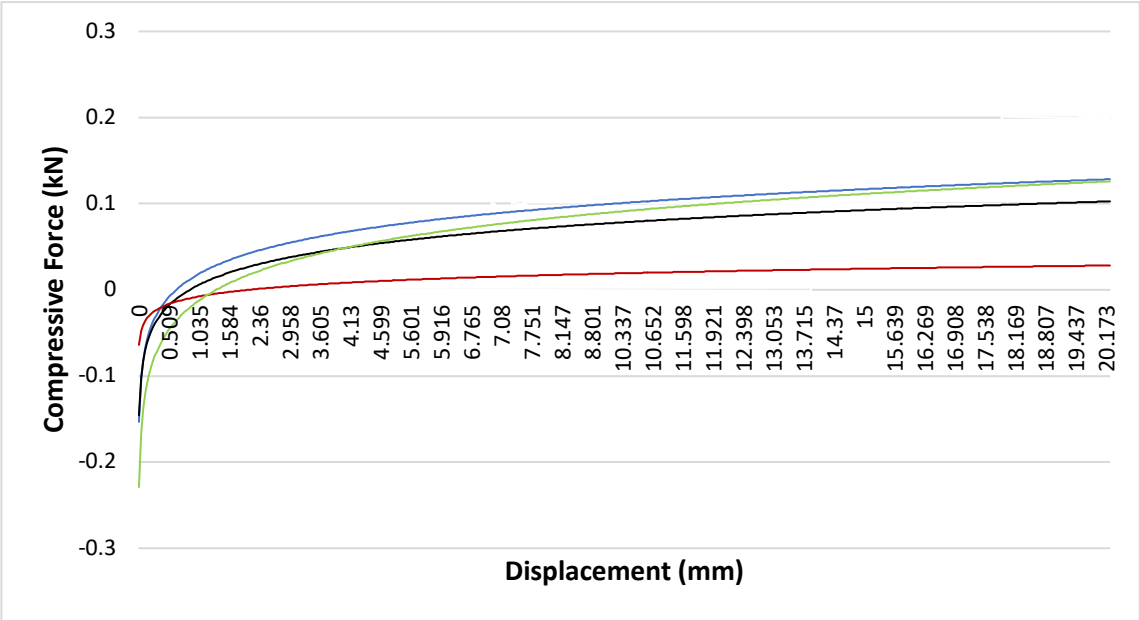

Figure 49: Wet crush comparison of tested samples

Figure 49 shows the average wet crush compression performance of the samples. It is evident that all samples follow a similar loading pattern. As evident from the plateau region of the graph and the visual observation of the samples subjected to wet crush compression, on reaching a certain load the samples lost their structural integrity and the water starts to get squeezed out of the bandage layers before maximum loading was reached. The samples lost a significant amount of absorbed water during the loading as layers got compressed. However, after a significant water loss, the samples underwent failure at the highest loading value. Close visual observation of the samples after failure, showed that the layers have delaminated at failure and most of the absorbed water was removed.

Discussion:

Samples when wetted, absorb water, hydrating $CaSO_4$ into $CaSO_4.2H_2O$. Water is absorbed by the binder and underlying bandage layers as well. This causes swelling in the dried bandage layers making the bandage loose structural integrity. Upon mechanical compression, water absorbed by the underlying bandage and binder are squeezed out, leaving $CaSO_4.2H_2O$. The loss of structural integrity with water absorption and the sudden loss of water due to compression causes delamination between the bandages as well as collapse of the hollow cylinder walls causing failure.

When it comes to RHA replacement samples, RHA shows comparatively good water-resistant properties as discussed under 5.5.3, but RH particles present absorbs free water and undergo swelling owing to prolonged immersion. Thus, excessive addition of RHA results in higher water absorption values, leading to poor performance. The 7-day behavior of 5% RHA samples is evident through wet crush compression as the amount of water absorbed upon submersion is less due to the lower wettability of the RHA particles and the reduced number of unhydrated zones. Further, the microstructure shows that compared to other RHA blends the amount of plaster crystal formation on top of the RHA particles are lower in density.

At the 7-day mark, 5% RHA modified samples have gained significant compressive strength with a much denser crystal structure with minimal unhydrated plaster in the mix, this is seen from the lower water absorption upon immersion. However, 10% RHA samples have a slightly higher volume number of unhydrated plaster. These undergo

hydration upon immersion by attracting more water. However, the previously trapped free water, also contributes to hydration of unhydrated $CaSO_4$. Owing to this crystal formation, the composite experiences a surge in compressive strength. Compression of the hydrated plaster pushes out the excess free water from the samples and this causes loading to continue.

Similar observation was seen in the 15% RHA modified samples as stated under 5.4.1, higher degree of unhydrated plaster, higher crack widths and higher RHA particles per unit volume results in a decrease in wet crush performance. The load values retain until the free water is forced out of the samples.

All samples lose their structural integrity very early on and reach a plateau phase where loading sustains. This loading can be crudely utilized as the maximum load that a sample can withstand even after wetting before losing its structural integrity.

5.5.6 Investigation of the tensile strength of samples

Introduction:

Tensile strength test help assess the ability of orthopedic plaster to withstand stretching or tension forces. While compression strength is more relevant for evaluating how plaster resists compression, tensile strength measures its resistance to being pulled apart. As orthopedic plaster is bound to the underlying cotton bandage, the bandage anisotropy affects the overall elongation properties. Therefore, tensile strength is crucial to provide a comprehensive understanding of the overall mechanical characteristics.

For this study, ASTM D751 for evaluating tensile strength and elongation of coated fabrics was modified to test the tensile strength of plaster coated bandages. Plaster coated bandages gain its tensile property, mainly due to the underlying fabric along with the adhered plaster coating.

Sample Preparation and Test Method:

On average a plaster coated bandage has a thickness of 3mm. The samples were layered up to 5 layers (*the minimum thickness for a light to moderate weight bearing cast*). This thickness eliminates outliers to results due to delamination between layers and thickness modifications due to hydration products forming in between layers.

The dimensions of the samples were decided based on; ASTM D751 standards, the material limitations and the minimum gripping requirement of the INSTRON Dynacell.

To layer up, the samples were dipped in water at room temperature (20 -25 °C) and lightly squeezed to remove excess water. Special care was provided to ensure good lamination between layers and kept under compression until cured (3 hours). The samples were allowed to dry for 7 days under room temperature.

Upon drying, the samples were cut using a pair of scissors along the bandage role direction (horizontally), as elongation is better along the bandage. Piping made of grade 40 sand paper was fitted at each gripping end. This ensured a good grip at the gripping jaws of the Dynacell. Figure 50 shows the dimensions of the samples prepared, including the gripping ends. 3 samples were prepared from each category for testing.

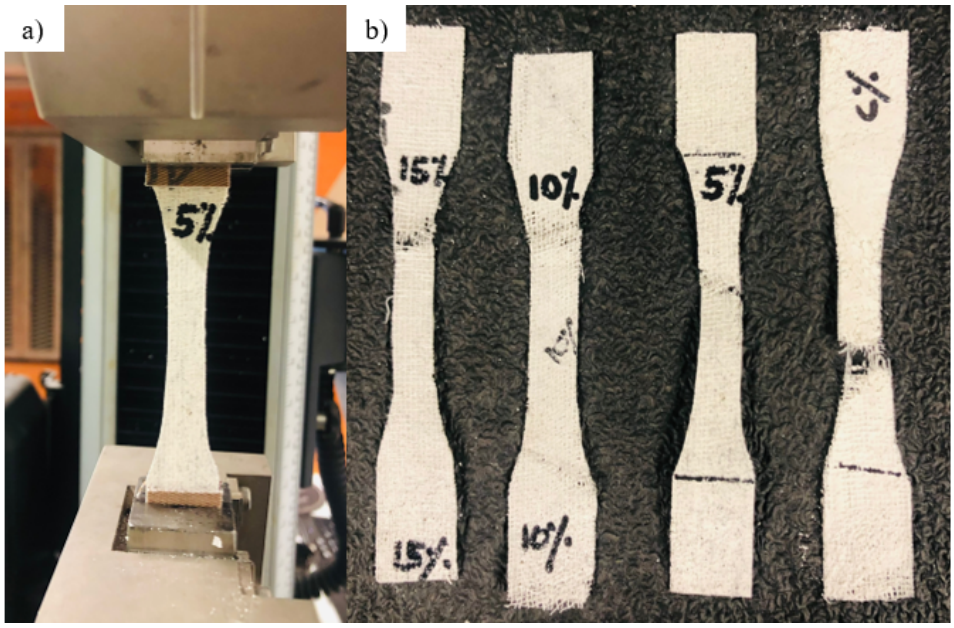

Figure 50: a) How the test samples are fitted to the Dynacell b) The sample test specimens

The samples were fitted to the load frame using the conventional testing grips (grip to grip distance set to 70mm) and were stretched at a constant rate of 1mm/min. Stretching was done until total failure and delamination of the specimens occurred. The force was recorded at 100Hz using a 5kN load cell (INSTRON, Dynacell) accurate to 0.05%. The force-elongation graph of each test was plotted to identify the load at failure (ultimate failure load and the ultimate tensile load).

Ultimate tensile stress was calculated according to;

$$\textbf{Ultimate tensile stress}(\sigma_t) = \frac{\textbf{Force at Failure (F)}}{\textbf{Cross} - \textbf{sectional Area } (A)}$$

For higher reliability of the stress calculations the thickness and width of the central portion of each sample was averaged over three measurements; one at center of sample and two more locations equally spaced from the center.

Results and Analysis:

The averaged value of the force- elongation graph is shown under Figure ***. All control samples, 10% RHA and 15% RHA modified samples failed at loads slightly lower than the ultimate tensile load. However, 5% RHA modified samples failed at ultimate tensile loading of 0.0417kN.

Apart from 5% RHA modified samples both 10% RHA and 15% RHA samples performed lower than the control sample. The ultimate tensile loads were equal to 0.0394kN for control, 0.0417kN for 5% RHA, 0.0378kN for 10% RHA and 0.0283kN for 15% RHA respectively. 5.8% tensile strength gain was recorded in 5% RHA samples comparative to the control with 4.1% and 28.2% strength reductions in both 10% RHA and 15% RHA samples.

As the underlying bandage contributes significantly to the tensile strength along the bandage, it is necessary to quantify the degree of tensile strength in this direction on 5 ply virgin cotton bandages. Thus, the tensile strength of the bandage in tension was 2.001MPa or 0.0242kN. Which is 37.27% of the tensile strength of the control.

Table 21: Ultimate tensile strength and load at failure of tested samples

Specimen Category	Ultimate Tensile Strength (Mpa)	Load at Failure (kN)
Control	3.175	0.0394
RHA 5%	3.475	0.0417
RHA 10%	3.15	0.0378
RHA 15%	2.333	0.0283
Bandage (5 ply)	2.001	0.0242

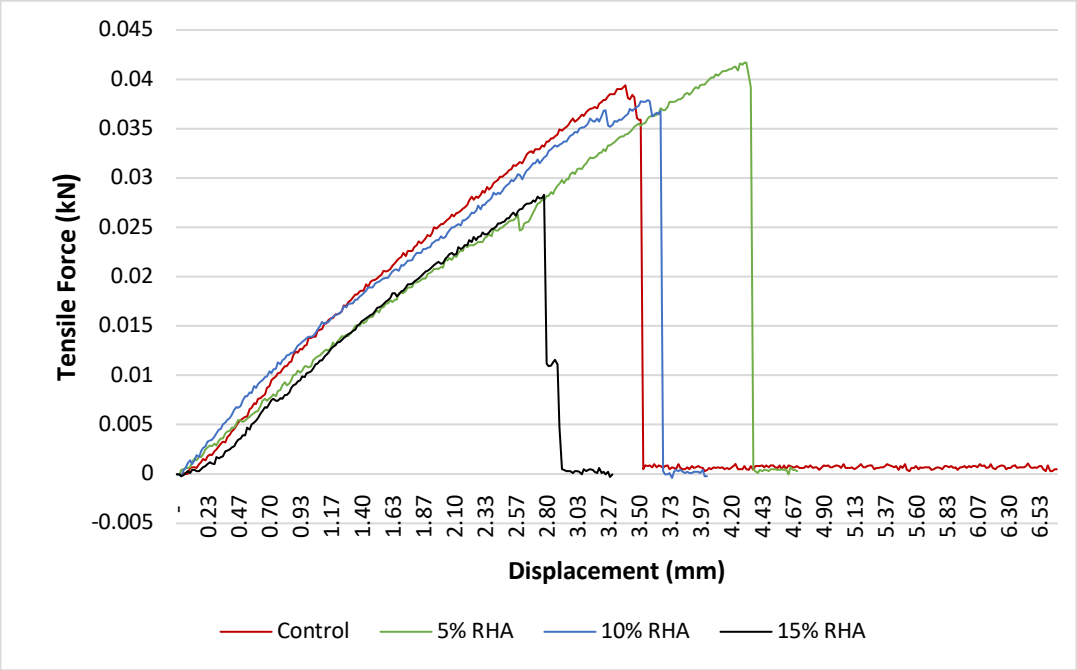

Figure 51: Comparison of tensile loading of samples

Discussion:

Through visual observation and results obtained, it is evident that the bandage contributes largely to the tensile strength along the direction of the bandage. The binder adheres the mix on to the base bandage layer. Thus, increased RHA additions can cause significant material loss from the bandage when pulling forces are applied. This is due to the excess

unburnt RH particles and carbon present. When the RHA replacement is at 15%, significant material loss was seen during tension. Higher presence of unhydrated $CaSO_4$ in the samples, cause the material to flake off faster. Owing to this material loss and performance of the base plaster lower performance at tension was seen compared to the control. Samples with higher crystal formation on top of RHA particles performed poor in tension due to faster flake off of the $CaSO_4$ during tension.

Owing to good binder adhesion, lower crystal growth on top of RHA particles, lesser volume of unhydarted plaster, 5% RHA modified samples performed better at tension. Plaster blends cannot be subjected to tension due to early breakoff and extreme poor performance in tension, only bandage samples can be subjected to tension. In case a highly elastic base bandage was used, tension performance of the resultant sample can significantly improve.

5.6 Thermal Performance Analysis

5.6.1 Investigation on heat of reaction

Introduction:

Burns on skin and heat entrapment after application of plaster bandages are widely reported due to the exothermic hydration reaction of plaster when curing [27]. This is critical in pediatric and elderly fracture management due to the elevated skin sensitivity.

When plaster casts are fitted to patients, the cast is laid on top of the padding layers applied to the appendage. This can trap a significant amount of heat apart from the heat generated

by the body. If the bandage also contributes significantly during setting, this can contribute to higher heat entrapment.

To evaluate the possibility of burns from the heat produced by the bandage, isothermal calorimetry is a great tool. This evaluates the heat of hydration and continuously follow the reaction rate at different stages of the complex hydration process.

This also analyses the effect of temperature on the hydration process and detects any incompatibility of the material.

Although not as complex as the hydration of cement, POP hydration also shows complexity as the mixes are not pure POP but contains other admixes. However, the predominant heat release is due to $CaSO_4$ hydration.

Isothermal calorimetry provides insight on how different blends hydrate and how different hydration products affect the mechanical properties of the end product. In this study the rate of hydration and heat of the plaster mixes upon application to the patient are evaluated.

Usually patients take up to 2 to 5 days to get adjusted to being placed in a fracture cast and any superficial burns and heat related discomfort is experienced during this time. Further, the skin covering the fracture location is damaged, inflamed and highly sensitive during this period.

Sample preparation and Test Method:

20g of wet plaster mix from each blend were placed in 20mL ampoules and the cap was fitted as shown below. Sample preparation was done according to ASTM C1679 for cement hydration. This was slightly modified to suite the plaster blends.

The TAM Air 8 -channel Isothermal calorimeter was used for testing, which has an air-based thermostat and can simultaneously evaluate up to 8 samples over a course of days to weeks.

The marked ampoules were loaded into the TAM Air and allowed to be tested continuously over a period of 72 hours / 3 days.

The heat flow vs time and heat vs time plots were obtained for analysis.

Results and Analysis:

The below graph shows the Heat (J) vs Time (s) of the samples subjected to isothermal calorimetry over a period of 48 h.

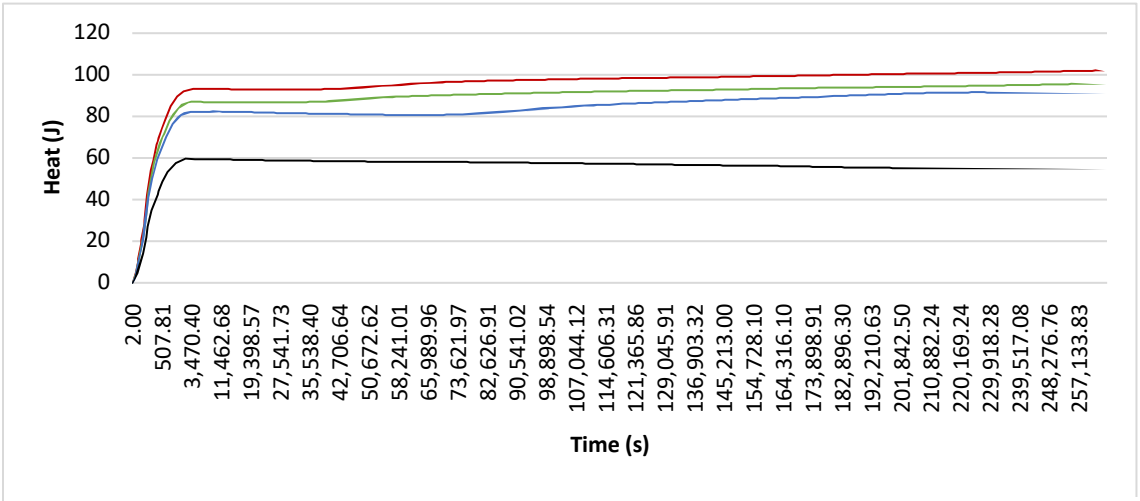

Figure 52: Heat of hydration of tested samples

As per the above graphs, the heat of hydration of the control sample is higher than the RHA replacements. In undergoing hydration, the peak of the heat flow must be higher due to the formation of the hydration product, which is $CaSO_4.2H_2O$, which then converts into $CaSO_4$ as the water evaporates setting the plaster. However, the RHA samples show lower hydration peaks compared to the control, which shows that the RHA particles trap water required for hydration. As the RHA percentage increases the amount of free water entrapped is higher, therefore the heat of hydration reduces according to Figure 52.

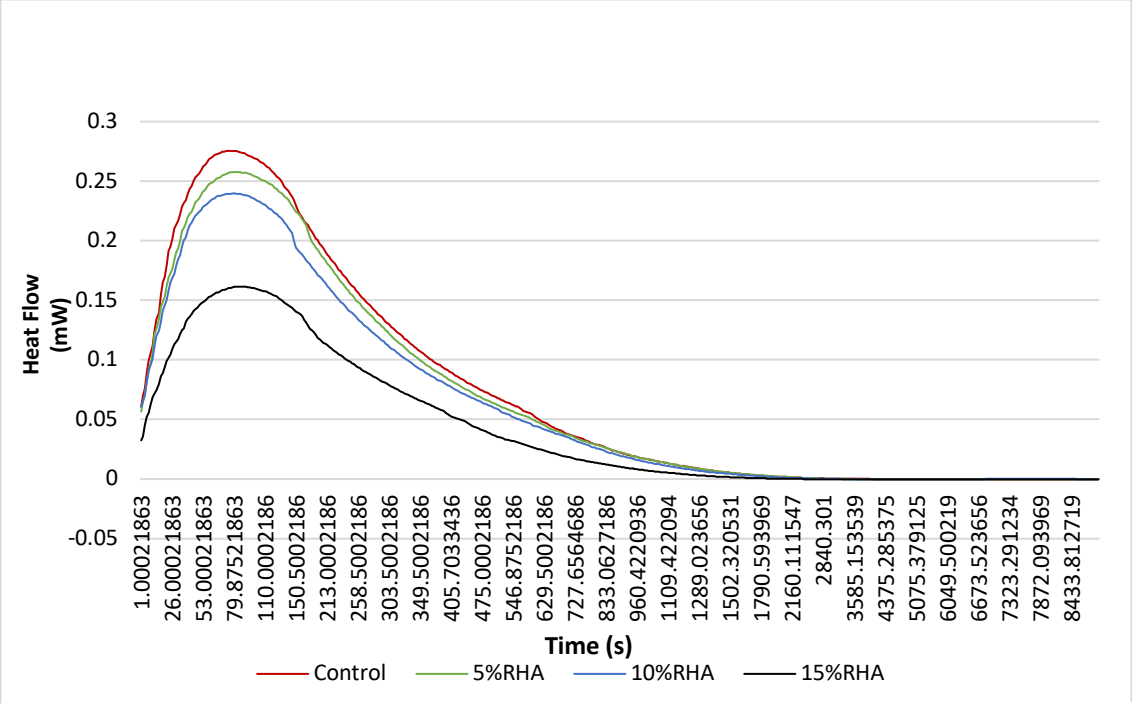

Figure 53: Comparison of heat flow of tested samples

On close observation of the control sample (Refer Figure 54), a peak is observed at approximately 10 minutes. According to literature, this refers to the beginning of plaster setting as the $CaSO_4.2H_2O$ is saturated at this point. However, Vicat tests showed that

plaster setting time was around 15 minutes for the control. This difference was mainly owing to the fact that the samples used for isothermal calorimetry were paste of the blends, not bandage samples. The base bandage can retain a significant amount of water, lengthening the setting time.

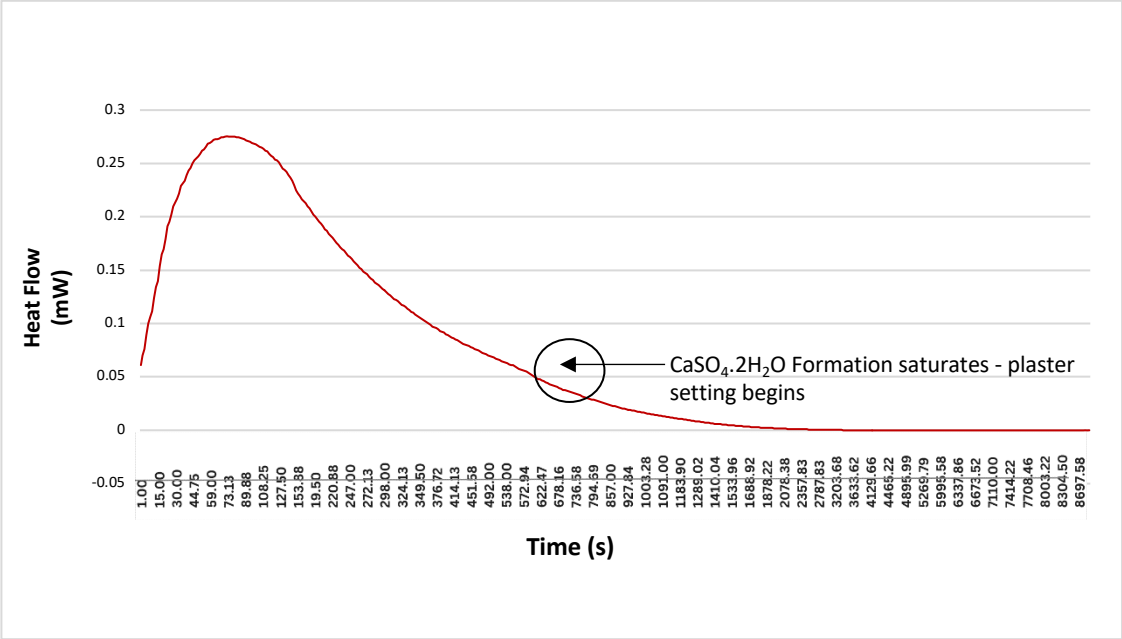

Figure 54: Heat flow vs time of the control

Similar peaks were observed in the 5% RHA and 10% RHA samples, however the peak diminishes as the RHA content increases and was not visible in the 15% RHA sample. The diminished peak height and the $CaSO_4.2H_2O$ saturation peak shows that as RHA percentage increases the heat of hydration reduces due to RHA particles depriving free water required for hydration.

However, this transfers in to improved patient comfort as the heat generation is reduced, but at the cost of reduced mechanical strength.

Discussion:

The heat vs time curves show that with the adequate availability of free water for $CaSO_4$ hydration, the heat of hydration increases. Control samples receive adequate water to undergo crystal formation (SEM images prove this), thus higher heat is emanated. However, as RHA percentage increases the heat of hydration reduces. This provides early thermal comfort for the patient, especially for pediatric and elderly patient fracture care.

This coupled with the S_{BET} micropore results show that the 5% RHA samples offer near equal thermal comfort to the control. Although early heat of reaction is reduced in 10% and 15% RHA samples, their micropore volumes and S_{BET} are reduced, which makes it difficult for bi-directional heat exchange and cast breathability after immobilization.

5.6.2 Investigation of heat conductivity and thermal effusivity

Introduction:

To analyze the heat exchanging nature of orthopedic plaster and modified plaster blends, thermal conductivity and thermal effusivity are important parameters.

Thermal conductivity is important due to its influence on temperature regulation within the cast and its impact on patient comfort and safety.

When casts are worn over extended periods, maintaining a stable temperature within the cast is crucial for patient comfort. Therefore, proper thermal conductivity helps in efficiently distributing and regulating the temperature, preventing discomfort caused by excessive heat or cold, particularly for long body and hip spica casts. Good thermal conductivity avoids localization of hot and cold spots that can decrease blood circulation

over time and effective for moisture control. As the skin sweats the skin emanates heat towards the cast and thermal conductivity is essential to manage moisture and reduce the complications of skin softening and bacterial growth.

Further, this avoids superficial thermal injuries, due to plaster exotherm at early application and heat entrapment after being fitted to the cast.

Thermal effusivity is a measure of how quickly a material can exchange thermal energy with its surroundings. This is crucial to allow quick exchange of heat due to plaster exotherm as well as to evaporate moisture from the cast. This parameter assists in regulating body temperature, prevention of sweat accumulation, skin maceration and to avoid discomfort due to long term immobilization.

Thermal conductivity and effusivity were tested using the C-Therm TCi Thermal Conductivity Analyzer, which uses Modified Transient Plane Source (MTPS) technique. A one-sided, interfacial heat reflectance sensor applies a constant heat source to the sample and based on the rate of voltage drop of the sensor element thermo physical properties of the sample were calculated.

Sample preparation and Test Method:

According to the minimum requirements for the C-Therm TCi Thermal Conductivity Analyzer, a minimum sample thickness of 17mm was maintained.

Hence, 20mm thick, 40cmx 40cm samples were casted using the plaster blends. All samples were smoothened to achieve a flat and even surface.

C-Therm TCi Thermal Conductivity Analyzer sensor was prepped by applying thermal paste on the senor to ensure proper and even contact between the sample and sensor interface. The prepared samples were placed on the sensor as shown by Figure

Each sample was subjected to a minimum of 5 test cycles with a test time of 0.8 to 2.5 seconds on average. The sensor is highly sensitive and was able to detect fine changes in material inhomogeneity. To overcome this, 5 test cycles were run on five identified points on each sample as shown under Figure 55.

The software interface was used to calculate the thermal conductivity and thermal effusivity values based on the real time data graphed.

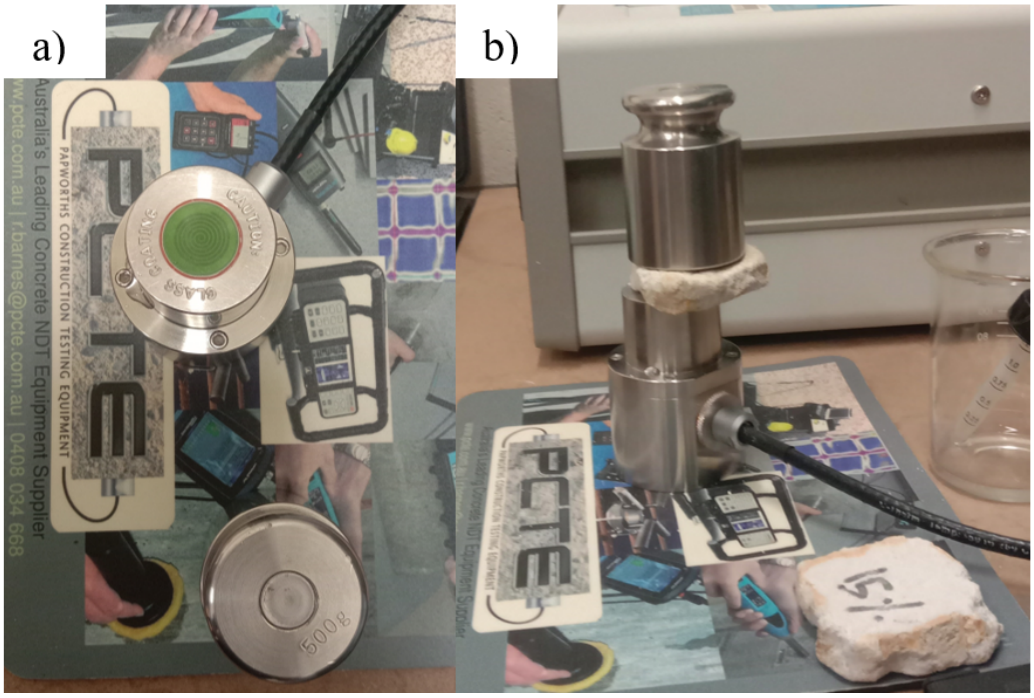

Figure 55: a) the sensor of the C-Therm TCi b) sample placement for thermal conductivity studies

Results and Analysis:

The following table, denotes the Thermal conductivity and Thermal effusivity values for the samples tested;

Table 22: Thermal conductivity and effusivity of tested samples

Specimen type		Effusivity [$Ws^{1/2}/ m^2K$]	Conductivity (W/mK)
Control	C-1	692	0.35
	C-2	687	0.35
	C-3	688	0.35
	C-4	687	0.35
	C-5	687	0.35
Average	C_{avg}	688.2	0.35
RHA-5	R5-1	695	0.35
	R5-2	695	0.35
	R5-3	693	0.35
	R5-4	696	0.35
	R5-5	697	0.35
Average	$R5_{avg}$	695.2	0.35
RHA-10	R10-1	519	0.21
	R10-2	508	0.2
	R10-3	508	0.2
	R10-4	507	0.2
	R10-5	508	0.2
Average	$R10_{avg}$	510	0.202
RHA-15	R15-1	442	0.15
	R15-2	434	0.14
	R15-3	435	0.14
	R15-4	436	0.14
	R15-5	436	0.14
Average	$R15_{avg}$	436.6	0.142

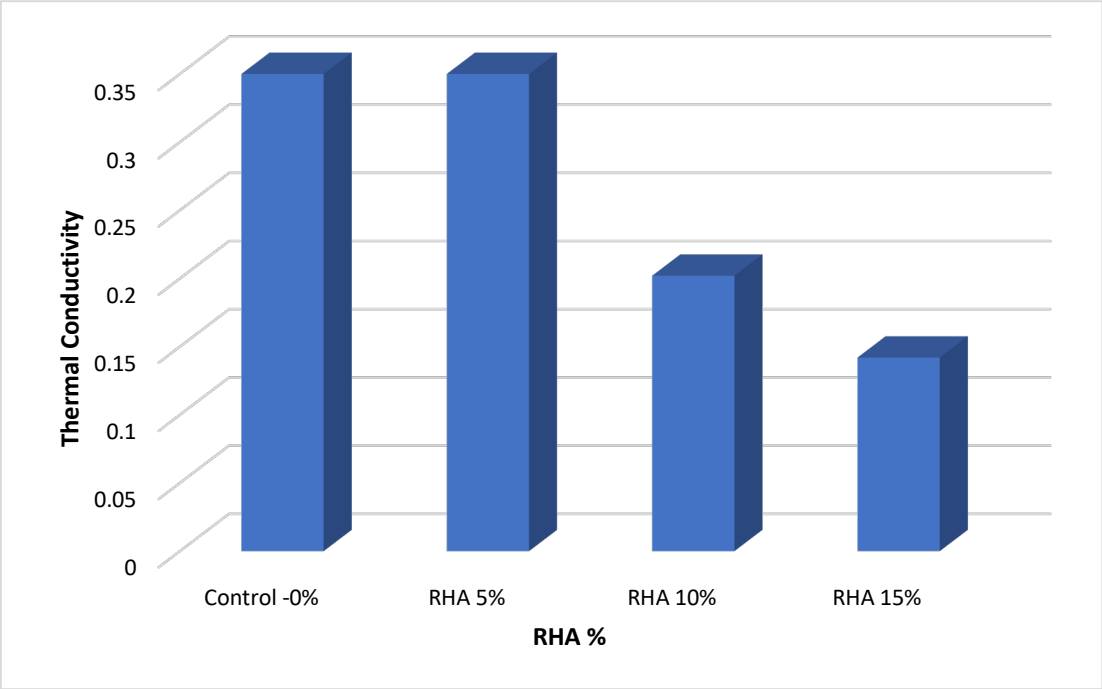

Figure 56: Thermal conductivity variation with variation in RHA %

Based on the results obtained the thermal conductivity values decrease as the RHA percentage increases. Higher RHA percentages register lower thermal conductivity values. However, the 5% RHA replacement specimen recorded the same thermal conductivity value of 0.35 W/mK as the control specimen. This shows that 5% RHA specimens were almost similar to the control. A 42.2% decrease in thermal conductivity was calculated in the 10%RHA specimen in comparison to the 5% RHA sample.

For the 15% RHA sample the decrease was a 85.8% in comparison to the 5%RHA sample.

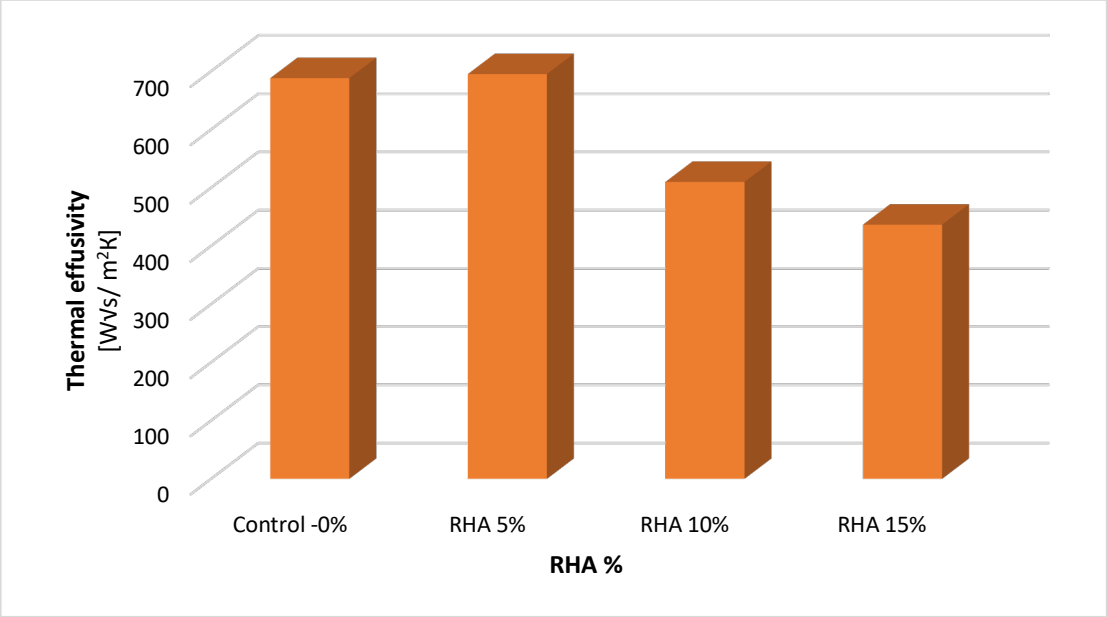

Figure 57:Thermal effusivity variation with variation in RHA %

The 5% RHA sample recorded higher thermal effusivity meaning it feels cooler to touch than other samples tested. The 5% RHA sample showed a 1.02% increase in thermal effusivity compared to the control. However, 10% RHA and 15% RHA replacement samples recorded 25.9% and 36.5% reductions in thermal effusivity than the control.

Figure 58 shows the variation of thermal conductivity variation of the samples in relation to their thermal effusivity.

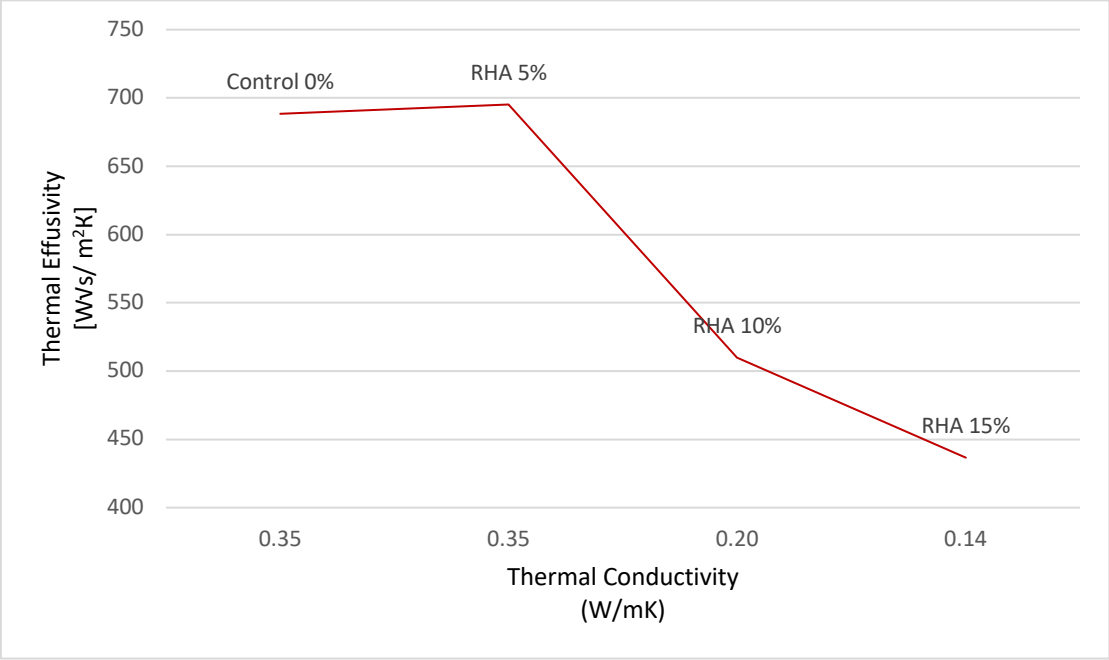

Figure 58: Thermal effusivity vs thermal conductivity of tested samples

Thus, based on the above graph it is evident that 5% RHA replacement performed better in terms of thermal conductivity and thermal effusivity values. As higher insulating properties although would prevent burns due to early heat, this can cause higher discomfort when body heat cannot be effectively conducted overtime, thus leading to heat sores and skin maceration in patients.

Discussion:

Thermal conductivity values obtained claim that as the RHA % increases, the material becomes a good thermal insulator. Therefore, making the heat transfer towards the underlying skin much lower, providing high thermal comfort from the exothermic hydration process of plaster. Thus, making RHA modified plaster, ideal to prevent burns

due to early heat of the plaster setting process. However, in transferring heat generated by the body to the atmosphere and increasing cast breathability, such lower conductivity values can cause heat entrapment leading to skin maceration and decreasing patient comfort.

Thermal conductivity varies significantly among materials and are highly dependent on the structure of the material. The S_{BET}, micropore diameter and SEM microstructure analysis shows that as the RHA % increases micropore volume reduces. However, higher crack widths and crack accumulation are seen surrounding the RHA particles. As the RHA % increases the crack widths have increased but the micropore diameter has greatly reduced. Thus, making 5% RHA modified samples a good candidate for thermal comfort than the 10% and 15% counterparts.

How the skin feels when placed in a plaster is essential as the thermoreceptors in the skin monitor and relay information to the brain about the things that come in contact. This is critical for patient comfort, especially when fitted to casts worn over a prolonged period of time. Thus, thermal effusivity is another important characteristic. The results obtained shows, as the thermal conductivity values reduced with increasing RHA percentage, the thermal effusivity values also dropped. Thus, similar to the thermal conductivity analysis, 5% RHA modified samples are good candidates for thermal comfort than the remaining RHA modified samples. As the base bandage was eliminated in developing the samples the effect of cotton bandages on thermal conductivity and effusivity wasn't considered here.

5.7 Theoretical verification of heat of reaction

Steady state conduction through multiple cylindrical layers

This was done to verify the heat of reaction based on the obtained thermal conductivity values obtained through the C-Therm testing.Although the prepared samples when applied as a bandage on top of the padding layer has many layers (minimum 5), this analysis assumes all the plaster layers as a single unit.

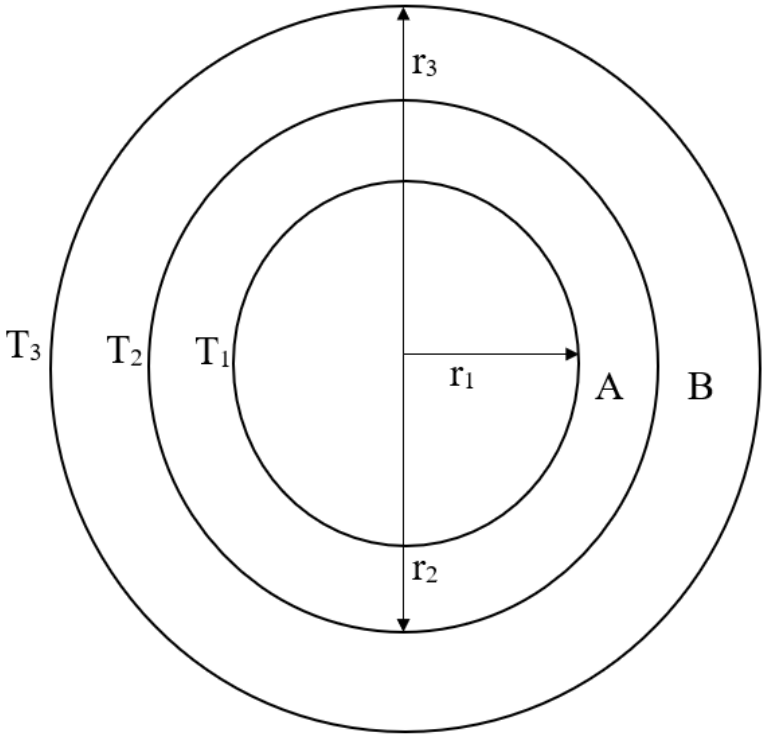

Figure 59: Steady state heat transfer through multiple cylindrical layers

A- Padding layer

B- Plaster

Heat transfer mechanism- conduction

$$Q = \frac{T_1 - T_2}{R_{padding}} = \frac{T_2 - T_3}{R_{plaster}}$$

$$R_{padding} = \frac{r_2 - r_1}{K_{padding}\ A_{l_n padding}}$$

$$R_{plaster} = \frac{r_3 - r_2}{K_{plaster}\ A_{l_n plaster}}$$

$$A_{l_n padding} = \frac{A_2 - A_1}{l_n(\frac{A_2}{A_1})}$$

$$A_{l_n plaster} = \frac{A_3 - A_2}{l_n(\frac{A_3}{A_2})}$$

The cross-sectional areas are;

$$A_1 = 2\pi L r_1$$

$$A_2 = 2\pi L r_2$$

$$A_3 = 2\pi L r_3$$

$$T_1 - T_2 = Q R_{padding}$$

$$T_2 - T_3 = Q R_{plaster}$$

$$T_1 - T_3 = Q\ (R_{padding} + R_{plaster}\ )$$

$$Q = \frac{T_1 - T_3}{R_{padding} + R_{plaster}}$$

Thus, the following Q values can be obtained;

Table 23: Heat flow values of heat of hydration, theoretically calculated

Sample Category	T_1-T_3	Thermal conductivity (K)	$R_{padding}$ +$R_{plaster}$	Q (J)
control	0.8	0.35	0.00911391	87.777886
RHA 5	0.79	0.35	0.00911391	86.680662
RHA 10	0.88	0.21	0.01518985	57.933404
RHA 15	0.92	0.14	0.02278478	40.377827

According to the heat of hydration values obtained using isocalorimetry, the values closely follows the pattern observed in the graph shown under Figure52. 10- 5% RHA samples show a deviation with practically obtained values showing more than 40% increase in practically obtained values. This is mainly due to the theoretical model only assuming steady state conduction and the padding layer being taken to account, whereas the padding layer was not taken into consideration during testing.

However, this verifies that the observed pattern is similar in both practical and theoretical scenarios.

As the heat transfer and thermal comfort was not greatly enhanced by the developed RHA modified plaster bandages, no further verification modelling for heat transfer was carried out in this study.

5.8 Chapter Summary

This chapter focused on the performance evaluation of Rice Husk Ash (RHA)-modified orthopedic plaster blends, building on the optimized mix designs developed in Chapters 3 and 4. The study aimed to assess the mechanical and thermal properties of the RHA-modified plaster, with a particular emphasis on compressive strength, tensile strength,

thermal conductivity, and heat of hydration. The findings provide valuable insights into the suitability of RHA as a sustainable filler for orthopedic plaster applications.

1. The binder and RHA particles entrap water, depriving adequate hydration when RHA percentage increases.
2. RHA in the mix contributes to pozzolanic reaction in the presence of $Ca(OH)_2$ in the mix, but this is significantly less, sometimes negligible.
3. Syngenite forms in the presence of K2SO4 and syngenite cores enable methodical crystallization of the CaSO4.
4. With RHA presence crystal formation occurs in flake like short stubby crystals on top of the RHA particles.
5. Cracking occurs at inter transition zones between RHA particles and the rest of the mix, crack widths increase with higher RHA percentages.
6. SBET reduces as the RHA percentage increases but owing to presence of large macro cracks and voids the micropore radius of the RHA samples are higher.

Microstructurally 5% RHA modified samples show good packing density than other RHA counterparts. The SBET remains almost similar to the control for 5% RHA modified samples, thus they translate into good cast breathability.

As for the mechanical performance:

1. Weight and density reduce as the RHA percentage increases;

   Control>5% RHA>10%RHA>15%RHA
2. Setting time variation;

Control<5%RHA<10%RHA<15%RHA

3. Bead time;

   Control< 10% RHA<15% RHA< 5% RHA

4. Compressive strength;

   Control<15%RHA<5% RHA<10% RHA

The 5% RHA-modified samples demonstrated superior compressive strength, with a 56.49% increase compared to the control. However, higher RHA replacements (10% and 15%) showed a decline in strength, with 15% RHA samples recording a 79.76% reduction in compressive strength. This highlights the importance of optimizing RHA content to balance strength and material performance.

5. Wet crush strength;

   Control< 15%RHA<5% RHA< 10% RHA

The 5% and 10% RHA samples outperformed the control in wet crush strength, with 5% RHA samples showing a 6.14 times higher load-bearing capacity. This indicates improved water resistance, a critical factor for patient comfort and cast durability.

6. Tensile strength;

   15%RHA<10%RHA<Control<5%RHA

The 5% RHA samples also performed well in tensile strength tests, showing a 5.8% improvement over the control. In contrast, 10% and 15% RHA samples exhibited reduced tensile strength, primarily due to material flaking and poor adhesion to the bandage.

In case of thermal performance:

1. Heat of hydration:

   15%RHA<10%RHA<5%RHA<Control

The RHA-modified samples exhibited lower heat of hydration compared to the control, with 15% RHA samples showing the most significant reduction. This is beneficial for patient comfort, particularly in pediatric and elderly care, as it minimizes the risk of thermal burns during plaster setting.

2. Thermal conductivity:

   Control≥5%RHA>10%RHA>15%RHA

3. Thermal effusivity:

   Control≥5%RHA>10%RHA>15%RHA

The 5% RHA samples maintained thermal conductivity and effusivity values similar to the control, ensuring effective heat exchange and patient comfort. Higher RHA replacements (10% and 15%) showed reduced thermal conductivity, which, while beneficial for insulation, could lead to heat entrapment and discomfort over prolonged use.

The study successfully demonstrated the potential of RHA as a sustainable filler for orthopedic plaster, with 5% RHA replacement offering the best combination of mechanical and thermal properties. The findings underscore the importance of optimizing RHA content to achieve a balance between performance and patient comfort. Future work should focus on refining the mix design further, exploring alternative binders, and

evaluating long-term performance in clinical settings to ensure the viability of RHA-modified plaster for orthopedic applications.

Microstructurally 5% RHA modified samples show good packing density than other RHA counterparts. The SBET remains almost similar to the control for 5% RHA modified samples, thus they translate into good cast breathability.

CHAPTER 6- CONCLUSIONS AND FUTURE WORK

6.1 Introduction

Although plaster casts are known to possess higher breathability than synthetic casts, patients still suffer from irritation, scratching under the cast and pressure sores. Addition of sustainable eco-friendly material such as RHA into plaster of pairs for development of orthopedic casts, possess a higher potential of improving the thermal comfort and mechanical strength. Further, the study was carried out to determine the mechanical strength gain of the RHA plaster, along with the microstructural changes plaster undergo after the addition of RHA, binders and nucleators.

The research aims to develop a biodegradable composite cast by replacing a percentage of plaster of paris with the sustainable agricultural by product Rice Husk Ash (RHA), to provide better patient comfort (Thermal comfort and cast breathability), lightweight, resistance to water degradation and improved mechanical strength. Through this study 5% -15% RHA modified plaster blends were developed in the form of paste and bandages and subjected to a series of mechanical and thermal tests. The microstructure of each category was observed to reach definitive conclusions.

Conclusions drawn from each chapter are presented here;

6.2 Conclusions from Chapter 2

Based on the literature review carried out under Chapter 2 the following conclusions can be made:

1. Historical Development: The evolution of immobilization materials dates back to 3000 BC, from splints designed from sticks and palm fiber bandages, gradually transitioning to plaster by 1798. Developments in fracture immobilization have taken place considering patient satisfaction, mobility and better mechanical properties.
2. Material properties: Even though new materials such as polyurethane impregnated fiberglass, polyurethane resin, thermoplastics and silicone rubber are available, the most favoured and cost-effective solution for immobilization is orthopedic plaster.
3. An immobilization material should possess required material properties such as adequate mechanical strength with tensile strength > 20 MPa, flexural modulus >2 kN/mm^2 and failure loads >10kN with the ability to bear cyclic loads, faster setting times, waterproofing ability and quick drying time, faster and less messy application, composition of non-toxic, non-flammable and non-irritant constituents that can be activated using low heat or undergo mild to moderate exothermic reactions when immersed in water, good cast breathability and vapor permeability, ability to accommodate swelling and edema, ability to be used in long term immobilization (exceeding 4 weeks), excellent conformity with no pressure point generation, good radiographical properties and economic feasibility, for higher patient comfort and an efficient healing process. Out of the available materials the synthetic materials only satisfy the strength requirements.
4. Patient Comfort: Patient comfort is a compulsory factor in long-term immobilization. Breathability, thermal comfort, water resistance, lightweight and

non –toxicity (non-irritant) are critical for patient comfort. Woodcast, a biodegradable material, shows promise but is cost-prohibitive for widespread use.

5. Complications: The most common complications in fracture immobilization are skin irritation and maceration, pressure sores, thermal burns, soft tissue swelling and cast saw burns. These complications mainly occur due to early stage heat generation, low porosity, and low conformity to body contours of immobilization materials. Hence, it is important to consider these properties as the top most priority, in the process of developing an immobilization material.
6. Setting time is another key factor considered in the development of immobilization material. If a cast possesses a low setting time the patient can be discharged to his familiar environment which ensures the psychological well-being of the patient and is also beneficial to maximize routine activities. This can be achieved through the addition of accelerators in the development process of the cast material.
7. In comparison of the available cast material under low cost, patient comfort, lower cast complications and setting time, the following order of choice can be achieved arranged in ascending order:
    - Cost: plaster of paris< silicone rubber < fiberglass- plaster hybrid < thermoplastic < fiberglass < PU resin < Woodcast
    - Patient comfort: Silicone rubber< thermoplastics< plaster of paris< PU resin< fiberglass< Woodcast
    - Lower cast complications: synthetic casts < plaster of Paris

- Setting time: RECAST< thermoplastics< PU resin≤ Fiberglass < Woodcast<plaster+ fiberglass hybrid< plaster of paris < cellulose based material< Silicone rubber

(Properties can vary according to the brand and additives used.) (Refer Table 2)

8. Sustainable Additives: Further modifications to the existing orthopedic immobilization materials are required for superior strength gain, improved material characteristics, lightweight and superior patient comfort. Therefore, it is required to modify the abundantly used plaster cast material to gain the aforementioned properties. Graphene Oxide is considered in the work carried out in the University of Moratuwa to achieve this objective.
9. RHA is a good thermal insulator which can prevent the heat emanated from the plaster setting to cause thermal burns on adjacent skin. Thus, improving early thermal comfort.
10. RHA also reduces the density of the resulting in a light weight composite.
11. GO is known to act as a catalyst, improving nucleation and reducing cast setting times. The exemplary mechanical properties of GO have the potential to improve the mechanical strength of traditional plaster.
12. GO reduces the water permeability when wetted and maintains good dispersion in mixtures. Thus, reduces the water degradation of the overall composite

Thus, this fulfills the specific objective;

1. To carry out a detailed literature review to identify gaps in knowledge regarding improvements required to enhance patient comfort of plaster of Paris orthopedic cast material currently used in immobilization – fully fulfilled

6.3 Conclusions from Chapter 3

Chapter 3 elaborates on the optimization of the mix design, focusing mainly on the development of the control mix. Key conclusions include:

1. Control Mix development: As the commercially available plaster mix is a trade secret, this study developed the control mix from scratch after referring to the literature available on patented mixes for orthopedic plaster. The control mix was successfully replicated using α and β CaSO4 hemihydrates, K2SO4 as an accelerator, and PVA and HPMC as binders. Dichloromethane (DCM) was initially used as a solvent but was replaced due to toxicity concerns.
2. Additive Selection: The study investigates the viability of GO and RHA as sustainable filler material for partial replacement of plaster. However, based on the initial compression tests carried out GO was eliminated from the study, owing to its failure to provide a compressive strength gain. Literature points out that RHA addition to plaster lowers the early strength but later shows a steady gain in compressive strength with the initiation of the pozzolanic activity after 7-14 days. Under the preliminary investigation 5% of the additives by composition of plaster from the developed control mix was carried out, without completely replacing any

material. Therefore, the final study focuses on replacing a quantity of plaster with RHA.

3. Workability and Setting Time: Higher RHA content reduced workability and increased setting time, necessitating the use of superplasticizers to maintain adequate preparation and application times.

This fulfills the specific objectives;

2. To replicate/ develop the commercially available clinical orthopedic cast material for modification using suitable additives – crack the recipe of the commercial product -fully fulfilled
3. To conduct testing to determine the best suited material and their material properties among the fillers identified to improve mechanical properties and thermal performance of control– *Variable percentages of RHA and Graphene Oxide* – partially fulfilled

6.4 Conclusions from Chapter 4

Based on the RHA blends developed from 5% -30% RHA replacements, mix designs for 5%, 10% and 15% RHA replacements by weight were considered herein after for the study, as they delivered compressive strength results than the developed control mix. Compression testing on sample cubes were used under Chapters 3 and 4 to decide on the type of additive to be used in the modification of the standard plaster cast and what range of replacements were feasible for further testing.

Hence, it is concluded that RHA is to be used as the filler/ additive for the study and replacement % by weight of 5,10 and 15 are suitable for detailed testing and analysis for the microstructure, thermal testing and mechanical strength testing.

1. To conduct a microstructure analysis of the developed product samples.
2. To carry out mechanical and thermal performance analysis on the developed samples.
3. To provide a sustainable alternative to overcome the current drawbacks of the traditional plaster cast, suitable for clinical applications.

This fulfills the specific objectives;

3. To conduct testing to determine the best suited material and their material properties among the fillers identified to improve mechanical properties and thermal performance of control– *Variable percentages of RHA and Graphene Oxide (GO was excluded based on preliminary results)*– fully fulfilled

6.5 Conclusions from Chapter 5

Chapter 5 provided a comprehensive evaluation of the mechanical and thermal performance of RHA-modified plaster blends. Key conclusions include:

1. The binder and RHA particles entrap water, depriving adequate hydration when RHA percentage increases.
2. RHA in the mix contributes to pozzolanic reaction in the presence of $Ca(OH)_2$ in the mix, but this is significantly less, sometimes negligible.

3. Syngenite forms in the presence of K_2SO_4 and syngenite cores enable methodical crystallization of the $CaSO_4$.
4. With RHA presence crystal formation occurs in flake like short stubby crystals on top of the RHA particles.
5. Cracking occurs at inter transition zones between RHA particles and the rest of the mix, crack widths increase with higher RHA percentages.
6. S_{BET} reduces as the RHA percentage increases but owing to presence of large macro cracks and voids the micropore radius of the RHA samples are higher.

Microstructurally **5% RHA modified samples** show good packing density than other RHA counterparts. The S_{BET} remains almost similar to the control for 5% RHA modified samples, thus they translate into good cast breathability.

As for the mechanical performance analysis:

1. Weight and density reduce as the RHA percentage increases;

   Control>5% RHA>10%RHA>15%RHA
2. Setting time variation;

   Control<5%RHA<10%RHA<15%RHA
3. Bead time;

   Control< 10% RHA<15% RHA< 5% RHA
4. Compressive strength;

   Control<15%RHA<5% RHA<10% RHA

5% RHA samples showed a 56.49% increase in compressive strength compared to the control, while 15% RHA samples exhibited a 79.76% reduction.

5. Wet crush strength;

   Control< 15%RHA<5% RHA< 10% RHA

5% and 10% RHA samples outperformed the control, with 5% RHA samples showing a 6.14 times higher load-bearing capacity.

6. Tensile strength;

5% RHA samples demonstrated a 5.8% improvement in tensile strength, whereas 10% and 15% RHA samples showed reduced performance due to material flaking.15%RHA<10%RHA<Control<5%RHA

In case of thermal performance analysis:

1. Heat of hydration:

   15%RHA<10%RHA<5%RHA<Control

RHA-modified samples exhibited lower heat of hydration, with 15% RHA samples showing the most significant reduction. This is beneficial for preventing thermal burns during plaster setting.

2. Thermal conductivity:

   Control≥5%RHA>10%RHA>15%RHA

3. Thermal effusivity:

   Control≥5%RHA>10%RHA>15%RHA

5% RHA samples maintained thermal conductivity and effusivity values like the control, ensuring effective heat exchange and patient comfort. Higher RHA replacements (10% and 15%) showed reduced thermal conductivity, which could lead to heat entrapment and discomfort.

Thus, based on mechanical and thermal performance **5%RHA modified samples** perform better, with 10% RHA samples closely following. The performance evaluation conclusively proves that 15%RHA modified samples cannot deliver the required performance both mechanically and thermally.

As the 5% RHA blends show adequate thermal conductivity and mechanical strength gain in comparison to the control plaster bandages, it can be used in replacement of traditional orthopedic plasters. However, there is a possibility that if improved 10% RHA modified plasters can be used in hybrid with 5% RHA bandages to locations where mechanical strength characteristics are highly required. However, more developments are necessary to obtain better cast breathability and superior strength in RHA modified plaster blend samples.

This fulfills the specific objectives ;

4. To conduct a microstructure analysis of the developed product samples- fully fulfilled

5. To carry out mechanical and thermal performance analysis on the developed samples- fully fulfilled

6. To provide a sustainable alternative to overcome the current drawbacks of the traditional plaster cast, suitable for clinical applications – fully fulfilled

6.6 Proposed Application of the Developed Cast Material

The developed sustainable cast material comprising of 5% Rice Husk Ash (RHA), represents a sustainable augmentation to traditional Plaster of Paris (POP) and synthetic fiberglass-based orthopedic immobilization systems. This formulation closely augments traditional POP with a sustainable and cost beneficial additive, addressing its inherent limitations.

The main aim of this study was to develop a composite that addresses the significant drawbacks associated with traditional POP—such as, its poor mechanical strength, durability, water degradation, and limited patient comfort.

The final application of this cast material targets clinical settings which require lightweight, durable, and thermally safe immobilization options that are highly sustainable without significantly contributing to hospital waste. Such an alternative is crucial in long-term fracture immobilization for pediatric and geriatric patients, who are more vulnerable to cast-related complications such as burns, maceration, and pressure sores.

6.6.1 Design and Material Benefits

The developed cast material incorporates 5% RHA as a partial replacement for POP. Through experimental study conducted, the 5% RHA blend was identified as the optimal formulation, showing superior mechanical integrity and thermal performance over both

the control and other RHA incorporated blends of 10% and 15% . This blend exhibited favorable properties such as:

- Reduced weight (12.9% reduction in weight compared to the control): Lightweight contributes to improve patient mobility and comfort.
- Improved thermal conductivity and effusivity: Minimizing the risk of thermal burns during setting and similar performance in cast breathability during immobilization time. Cast breathability is highly dependent on the porosity of the underlying cast liner.
- Adequate compressive and tensile strength: Ensuring secure immobilization comparable to traditional POP.
- Resistance to water degradation: Although RHA blends are not 100% waterproof, it shows better resistance to degradation under moist conditions, comparative to traditional POP.

These properties make the cast suitable for applications in orthopedic clinics, trauma centers, and emergency departments where fast-setting, durable, and lightweight casts are essential for fracture care.

6.6.2 Implementation in Clinical Settings

The 5% RHA blend has been designed to seamlessly integrate into existing orthopedic workflows. It mimics the application technique used for standard POP bandages, requiring no additional tools or training for medical practitioners. Casts are applied over standard

stockinettes and padding, followed by the wet activation of the bandage and molding on the affected limb.

Given the improved mechanical performance and lighter weight, the 5% RHA bandages are particularly suited for:

- Outpatient fracture care- where quick turnaround is essential and has voluminous fracture turnover.
- Pediatric orthopedics- where lightweight and thermal comfort are critical for compliance and healing.
- Geriatric fracture management- where fragility and skin sensitivity are common issues.
- Developing healthcare systems- due to its cost-effectiveness and sustainable resource base that drives healthcare to be Net Zero by 2050.

In these settings, the reduced risk of burns and pressure sores, combined with ease of handling and transportation, making it suitable for wide-scale adoption.

6.6.3 Sustainability and Future Potential

The 5% RHA blends bear significant implications in terms of environmental sustainability. RHA is an agricultural byproduct, abundantly available in rice-producing countries, such as Sri Lanka, India, Vietnam, Thailand etc. The husk is generally discarded or subjected to open burn which can create large volumes of flyaway and ash contaminating the irrigation network and causing difficulty in breathing. Using RHA to

replace a percentage of the Calcium carbonate reduces the CO_2 emissions and cuts down the use of nonbiodegradable hazardous material such as fiberglass and thermoplastics reaching landfill.

Therefore, in potential applications, the cast material could be:

- Commercialized as a green orthopedic product aligned with global sustainability and net zero goals.
- Hybridized (with traditional POP,fiberglass or other sustainable blends) for anatomical regions that require different mechanical properties.
- Optimized further for waterproofing, making it viable for long-term use in active individuals.

Additionally, further research has to be carried out in combining RHA with other bio-based polymers or graphene derivatives to further enhance its performance while maintaining low environmental impact and cost benefit.

6.6.4 Economic Feasibility of the developed material

The economic comparison of 5% RHA-modified plaster with conventional immobilization materials is summarized below:

Table 24: Base material availability, cost and environmental impact of popularly used immobilization material.

Type of Immobilization Material	Base material/s	Cost per Unit (USD/kg)	Availability	Environmental Impact
Traditional plaster (POP)	Gypsum ($CaSO_4.2H_2O$)	0.5-1.5	High	High CO_2 emissions
Fiberglass	Fiberglass, Polyurethane resin	5-10	Moderate	Non-biodegradable
Plaster -Fiberglass Hybrid	Gypsum, Fiberglass, PU resin	3-6	Moderate	Partially recyclable
5% RHA modified plaster	Gypsum, RHA, PVA, PCE	0.8-2.0	High	Sustainable, low CO2 emissions

[Developed by author]

Although slightly more expensive than traditional POP, the 5% RHA blend offers substantial environmental benefits and maintains cost competitiveness compared to synthetic alternatives.

Manufacturing Cost and Energy Analysis

Table 25: Manufacturing cost and energy analysis for immobilization material popularly used in clinical settings.

Type of Immobilization Material	Production Process	Manufacturing cost (USD/m^2)	Energy Consumption
Traditional plaster (POP)	Drying, Grinding, Packaging	2-4	High
Fiberglass	Resin impregnation. Molding	8-12	Moderate-High
Plaster -Fiberglass Hybrid	Plaster layering, Fiberglass coating	5-9	Moderate

5% RHA modified plaster	Plaster preparation, RHA addition	3-5	Moderate

[Developed by author]

Performance–Cost Benefit Summary

Table 26: Performance-cost benefit summary of popularly used immobilization material

Type of Immobilization Material	Strength and Durability	Thermal Comfort	Water Resistance	Weight Reduction	Estimated Lifespan (weeks)	Overall Cost-Effectiveness
Traditional plaster (POP)	Poor	Moderate	Poor	Low	4-6	Low
Fiberglass	Good	Moderate-Poor	High	Moderate-High	8-10	Moderate
Plaster -Fiberglass Hybrid	Good	Moderate	Moderate-High	Moderate	6-8	Moderate
5% RHA modified plaster	Moderate	Moderate	Moderate	High	6-8	Moderate-High

[Developed by author]

A holistic performance assessment shows that 5% RHA–modified plaster strikes a favorable balance between mechanical performance, environmental sustainability, and cost efficiency. The proposed RHA-modified cast material offers a significant advancement in orthopedic immobilization systems, combining effectiveness, safety, and environmental responsibility. By leveraging agricultural waste to enhance a conventional material, this solution integrates traditional practices with sustainable innovation. The 5% RHA bandage formulation provides an optimal balance of strength, comfort, and eco-efficiency, making it a strong candidate for widespread adoption across diverse healthcare environments.

6.6 Recommendations for future research

Based on the findings of this study, the following recommendations are proposed for future research:

1. Particle Size Optimization: Grading and grinding RHA to smaller particle sizes can improve homogeneity and reduce cracking at inter-transition zones. This can enhance the mechanical performance of RHA-modified plaster blends [24, 113].
2. Water-to-Plaster Ratio: Reducing the water-to-plaster ratio can minimize micropore formation, thereby improving mechanical strength and durability [26, 24].
3. Elastic Base Materials: Incorporating slightly elastic base materials instead of traditional cotton bandages can enhance tensile strength and extend the lifespan of the plaster cast [42, 43, 50].
4. Breathability Enhancement: Future studies should focus on improving the breathability of both the plaster cast and the underlying padding layer to enhance thermal comfort and reduce skin maceration [42, 47,50, 86].
5. Waterproofing: Developing waterproof coatings or additives that do not compromise breathability is critical for improving patient comfort and cast durability [4, 35, 47, 62].
6. Long-Term Clinical Studies: Conducting long-term clinical trials to evaluate the performance of RHA-modified plaster casts in real-world applications is essential for validating their suitability for widespread use [37, 73,81].

APPENDIX

Appendix 01: Comparison of modern-day immobilization material analyzed under the review

Material	Description	Activation	Cast layers required (10 cm wide)	Setting time	Curing time	Time for load bearing (s)	**General weight of cast (g)	x-ray permeability	Cost/ package ($)	
Plaster of Paris bandages	Plaster of Paris impregnated leno weave fabric bandage with accelerators and binders.	Dip 10s in water at 20-25°C	5-12 layers	4-8 mins to 30 mins * 4-8 mins for fast setting casts	24-48 hours	48-60 hours	>1000g	Radiopaque	$20	Rigid but brittle. Undergo water degradation and messy application. Suitable for long term immobilization.
Fiberglass - PU resin bandages	Polyurethane or PU resins impregnated fiberglass bandage	Dip water at 15-27°C for 2-10s	3-6 layers	3-5 mins	5-7 mins	15-30 mins	<500g	Radiolucent	$70-$89.	Rigid waterproof bandage contains isocyanates which can cause occupational asthma due to high dust generation during removal. Used as a secondary cast material.
Plaster of Paris , Fiberglass hybrid	Plaster of Paris casting tape overlaid with Fiberglass-PU bandage	Respective activation for each plaster of Paris and fiberglass bandages	4 layers of plaster overlaid with 4 layers of fiberglass bandage	Respective set times for each material. Total cast takes ~ 30 mins	Respective set times for each material. Total cast takes ~ 24 hours	Respective set times for each material. Total cast takes ~ 48 hours	>500g Depends on the number of layers	Radiopaque plaster layers	10% cost reduction compared to a total fiberglass cast.	Hybrid casts uses the benefits of both plaster and fiberglass but not radiolucent due to radiopaque plaster layers.
Polyester-PU resin and other PU resin bandages	Polyurethane polymer impregnated open weave polyester bandage (most common) *bandage type can vary	Cold water immersion	3-8 layers	3-5 mins	~30 mins	20-30 mins	~ 650g	Radiolucent As they are weaker than fiberglass require more layers, hence attenuates more	$158	Polyester offers more elongation and good flexibility to the cast. Contains isocyanates and tacky resins. Should handle using lubricated gloves. Used as a secondary cast material.

	according to commercial product.									
Thermo-plastic	Thermoplastic impregnated polyester tape with inorganic fillers. (available as thermoplastic impregnated bandages and thermoplastic sheets)	Immerse in hot water at 70-85°C for 1-5 mins	3-5 layers (~ 5 layers)	2-3 mins	3-30 mins	~15-30 mins	~700g	Radiolucent but shadows and artefacts present	< $56	Low temperature setting thermoplastics are available to reduce thermal damage. Low weight bearing ability than fiberglass bandages.
RTV Silicone rubber	RTV Silicone rubber + medical gauze with added curing agents and catalysts	Applied onto medical gauze until desired thickness is obtained and cut using bandage scissors to form the splint	2-5 layers	1 hour	2- 4 hours or 24 hours. Depends on curing agent used	~5-24 hours	450-600g	Splints are removed during radiological assessments	$ 12 per can	Absorbs impact forces and offers high flexibility. Used in short term (<4 hrs) splinting of sport related injuries. Not suitable for longer term circumferential casting
Woodcast	Woodchips from Finnish Aspen or Spruce in Biodegradable thermoplastic polymer matrix	Heated to 62°C	1 layer of 4mm material	15-30 mins when cooled at ambient temp (22°C)	15 mins	5-15 mins	Lightweight material. Exact weight not provided.	Good radiological properties, cast almost invisible in x-ray images	$71-$ 180	Sustainable Wood-plastic composite with good radiographical properties and rigidity. Can be reheated. No toxic materials available.
Cellulose based cast material	Pyroxylin +Boric acid impregnated fabric wetted by acetone	Cellulose impregnated bandage wetted using a quick drying solvent at room temperature	~ 3 layers	30-40 mins	Prolonged curing time	TBA	Lighter than plaster bandages	Radiolucent	TBA	Waterproof lightweight material. Prolonged drying times exceeding 30mins. Adequate ventilation required for cast drying. High flammability and shrinkage.

RECAST	Bio-based Poly Lactic Acid (PLA) plastic	Heated to 55-65°C	1 layers (thickness TBA)	After 3 mins	TBA	TBA	TBA	Radiolucent , exact details not provided so far	TBA	Biodegradable sustainable material, to reduce the number of synthetic cast waste ending in landfills.

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