Utilization of Waste Calcium Chloride ($CaCl_2$) for the Synthesis of Useful Chemicals

By

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Certificate

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Dedication

I dedicate this thesis to my loving Parents, Siblings & Teachers.

Abstract

Calcium chloride is waste of Solvay process, a process for manufacturing of sodium carbonate (soda ash) which is important raw material for many chemical industries. The discharged calcium chloride is either dumped to open land sites or is liquidated to the rivers where it causes environmental pollution. Calcium chloride discharge from the Solvay process can be used to produce calcium sulfate whiskers (CSWs). Environment friendly, cost effective and thermally stable CSWs have gained much attention as they are being extensively used as reinforcing material in pulp and paper, rubber, plastics and polymer composite materials.

In the first part, CSWs were prepared using sodium sulfate (Na_2SO_4) and calcium chloride ($CaCl_2$) discharged from the soda ash plant, by hydrothermal method. The study of different process parameters i.e. reaction temperature, molar ratio of reactants and mixing methods of reactants, was carried out and conditions were optimized for synthesis of CSWs. Based on these optimized conditions CSWs with high aspect ratio were made. The experimental results revealed that CSWs with length of 150-200 µm and width of 0.5 - 8 µm were produced by hydrothermal treatment of precursors that were formed by precipitation of Na_2SO_4 and $CaCl_2$ at temperature of 25 ^oC, having molar ratio of Na_2SO_4 to $CaCl_2$ 0.5:1and by adding Na_2SO_4 to $CaCl_2$. The morphology of whiskers was examined with the scanning electron microscope (SEM). The phase structures were identified by powder X-ray diffractometer (XRD). SEM results exhibited good morphology of CSWs and XRD provided phase identification.

In the second part, polycaprolactone-calcium sulfate whiskers (PCL-CSWs) composites were prepared to study reinforcing properties of CSWs in the polymer composites. Co-precipitation method was used for the synthesis of PCL-CSWs composites. The CSWs were added in different wt. percentages i.e. 5%, 10%, 15% and 20% to study the enhancement of mechanical properties of composite. The PCL alone was also used separately for comparison with the composites. To examine the mechanical strength two tests i.e. tensile test and flexural property test were performed by electronic universal testing machine (UTM). Mechanical test results were excellent and were comparable to literature. Process study provided optimum utilization of $CaCl_2$ to form CSWs that can be used as reinforcing material in polymer composites.

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Research Publications

Journal Paper

1. A. Rehman, S.H. Ansari, A. Hussain, Calcium Sulfate Whiskers: A review on preparation methodologies. (Under Review), International Journal of Materials and Product Technology, Inderscience.*

Conference Paper

2. M. Anees Ur Rehman, Ali Waqas, Shahid Hussain Ansari, Arshad Hussain. Synthesis of calcium sulfate whiskers from the waste calcium chloride by hydrothermal process, International Conference on Energy Systems and Policies, Nov 24th – 26th , 2014, Air University, Islamabad, Pakistan.**

*Annexure I

** Annexure II

List of abbreviation

CSW	Calcium Sulfate Whisker
PCL	Polycaprolactone
FGD	Flue Gas Sulfurization
PG	Phosphogypsum
CSD	Calcium Sulfate Dihydrate
CSH	Calcium Sulfate Hemihydrate
CS	Calcium Sulfate
PTFE	Polytetrafluoroethylene
THF	Tetrahydrofuran
RSS	Relative Supersaturation
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscope
UTM	Universal Testing Machine
UTS	Ultimate Tensile Strength
ISO	International Standard Organization
ASTM	American Society for Testing and Materials

Acknowledgment

I want to thanks Allah Almighty, The Most Beneficent The Most Merciful Who made me able to complete this project. No words are sufficient to express our gratitude to our devoted teachers for their exemplary patience, guidance and cooperation during the preparation of this thesis. I express my most truthful gratitude to Dr. Arshad Hussain, Engr. Shahid Hussain Ansari for their supervision. I also like to thank my whole GEC committee and Faculty members.

Chapter 1

Introduction

1.1 Background

Solvay process, named due to Ernest Solvay, is a synthetic process used for the production of sodium carbonate (Na_2CO_3). Sodium carbonate is commonly known as soda ash. Solvay process is also known as “ammonia soda process”. Sodium carbonate is a white, crystalline powder and is important raw material for production of glass, pulp and paper, soap and detergents, chemicals and many other industrial products [1]. Therefore, Solvay process is important synthetic process to manufacture sodium carbonate where natural sodium carbonates bearing brine or natural sodium carbonaceous minerals e.g. trona and nahcolite are not available. In 2012 the world’s soda ash production capacity was 63 million tons per year of which 45% was produced by Solvay process, 24% by natural trona and remaining 31% by other synthetic processes [2] as shown in Figure 1.1. The usage of sodium carbonate by % age is shown in Figure 1.2.

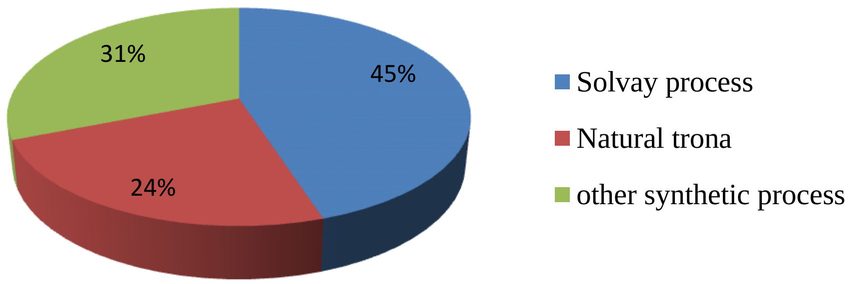

Figure 1.1. Production of sodium carbonate by different processes

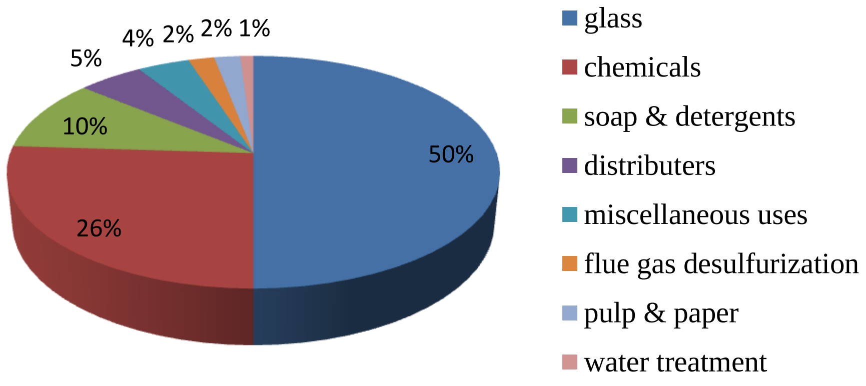

Figure 1.2. Applications of sodium carbonate in different processes

1.2 Solvay process

The raw materials for production of sodium carbonate in the Solvay process are sodium chloride (NaCl), calcium carbonate ($CaCO_3$) and ammonia (NH_3). The process can be summarized by overall reaction as shown in equation 1.1.

$$2NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2 \text{..................................} 1.1$$

It is a theoretical reaction and in practice it is not possible to manufacture the soda ash by above single step reaction. Therefore other substances and many processes are involved for the synthesis of Na_2CO_3. Figure 1.3 exhibits the process flow diagram for Solvay process.

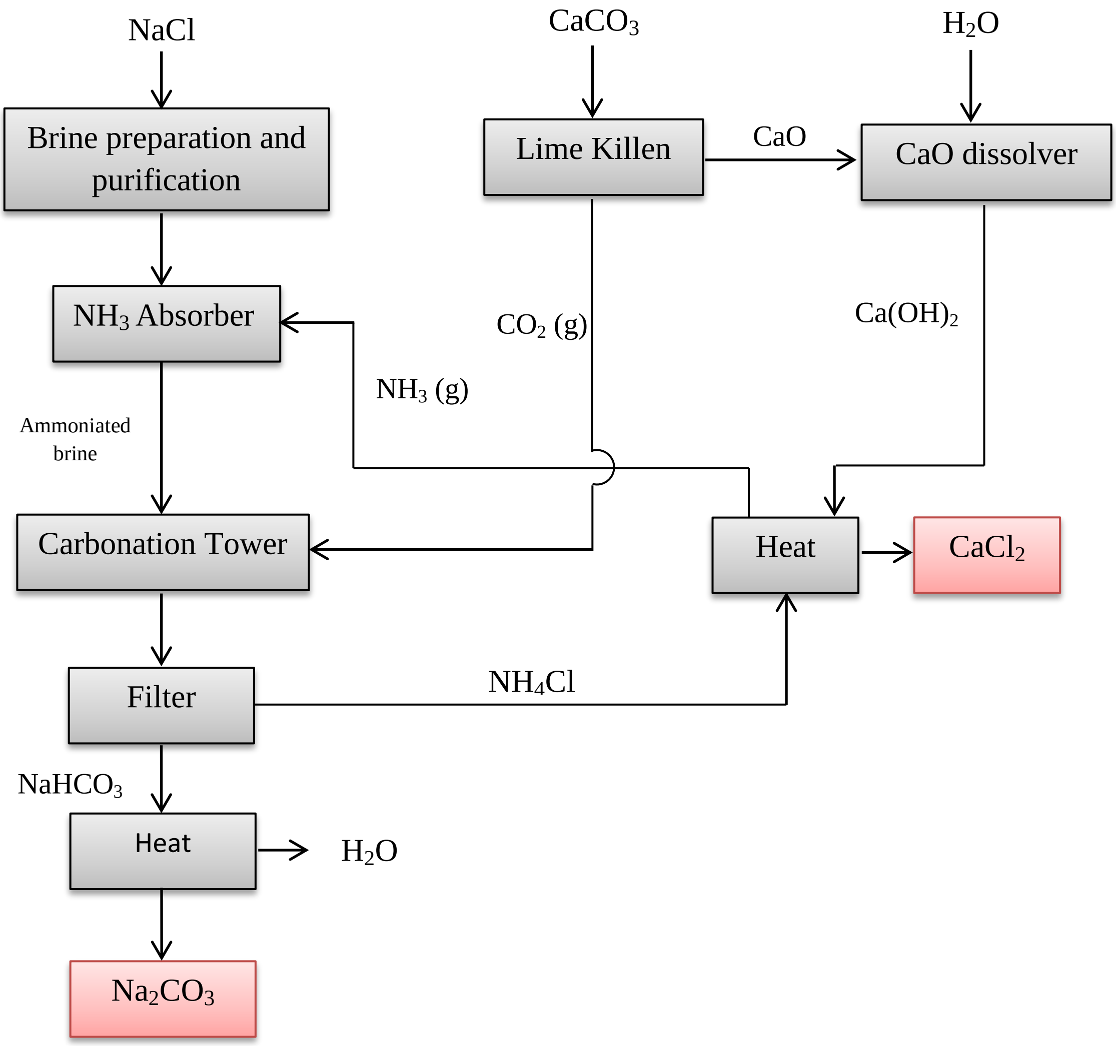

Figure 1.3. Block diagram for production of sodium carbonate by Solvay process

First of all NaCl brine is prepared either by solution mining of salt or by dissolving the NaCl salt in water and then purified from impurities such as magnesium and calcium salts. Then this brine is directed to the ammonia absorbers. As a first step of the process, ammonia (NH_3) is absorbed in the brine to saturate it (1), and then carbon dioxide (CO_2) is reacted with ammoniated brine to produce succeeding intermediates namely ammonium carbonate, $(NH_4)_2CO_3$ (2) and ammonium bicarbonate, NH_4HCO_3 (3). Sodium bicarbonate ($NaHCO_3$) and ammonium chloride (NH_4Cl) (4) are formed by continuous injection of carbon dioxide (CO_2) into the solution. Sodium bicarbonate is produced in crystals forms that are detached from the mother liquor (NH_4Cl) by filtration. After that the thermal decomposition of the $NaHCO_3$ produces Na_2CO_3, H_2O and CO_2 (5). Ammonium chloride (mother liquor) is then reacted with calcium hydroxide to recover ammonia (6). This gaseous ammonia is recycled to the absorption tower to produce ammoniated brine. Carbon dioxide (CO_2) and calcium oxide (CaO) (7) are produced by the calcination of calcium carbonate ($CaCO_3$), commonly known as limestone. Calcium oxide is converted into hydrated form, the calcium hydroxide also known as milk of lime (8) [3, 4]. Chemical reactions describing the above process are as follows:

$$\mathrm{NaCl(aq) + H_2O(l) + NH_3(g) \rightarrow NH_4OH(aq) + NaCl(aq)}\ldots\ldots\ldots\ldots 1.2$$

$$\mathrm{2NH_4OH(aq) + CO_2(g) \rightarrow (NH_4)_2CO_3(aq) + H_2O}\ldots\ldots\ldots\ldots\ldots\ldots 1.3$$

$$\mathrm{(NH_4)_2CO_3(aq) + CO_2(g) + H_2O \rightarrow 2NH_4CO_3}\ldots\ldots\ldots\ldots\ldots\ldots 1.4$$

$$\mathrm{2NH_4CO_3(aq) + 2NaCl(aq) \rightarrow NaHCO_3(s) + 2NH_4Cl(aq)}\ldots\ldots\ldots 1.5$$

$$\mathrm{2NaHCO_3(s) \rightarrow 2Na_2CO_3(s) + H_2O + CO_2(g)}\ldots\ldots\ldots\ldots\ldots\ldots 1.6$$

$$\mathrm{2NH_4Cl(aq) + Ca(OH)_2(aq) \rightarrow CaCl_2(aq) + 2NH_3(g) + 2H_2O}\ldots 1.7$$

$$\mathrm{CaCO_3(s) \rightarrow CaO(s) + CO_2(g)}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1.8$$

$$\mathrm{CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1.9$$

1.2.1 Solid waste from Solvay process

In Solvay process the recovery of ammonia is very important step that is accomplished by the reacting the mother liquor (NH_4Cl) with milk of lime $Ca(OH)_2$, which produces liquid suspension. The suspension so produced is known as distiller waste. This contains $CaCl_2$ and a small amount of unreacted NaCl. It is created in large quantities of about 10 m^3 per ton of soda ash produced. Distiller waste is the major problem for synthetic soda ash industry. It is normally directed to the settling basins where the suspended particles settle down at bottom of basins parted from the liquid phase. Clear overflow is dropped into the river, lake or sea which poses no appreciable problem. After evaporation the rest of water, solid sludge consisting of calcium chloride and small amount of sodium chloride is put away to open land sites which not only occupy useful land but also cause environmental hazards. If the suspension produced is pumped directly into the rivers, lakes, or other water streams, it raises the chloride ion concentration to a level which is unsafe for aqueous life. Figure 1.4 shows the waste bed of $CaCl_2$ on Shore of Onondaga Lake.

Figure 1.4. $CaCl_2$ waste located in waste bed along the shore of Onondaga Lake

1.3 Soda Ash industries in Pakistan

In Pakistan, following two industries are producing soda ash by synthetic Solvay process:

- ICI Pakistan Ltd.
- Olympia Chemicals Ltd.

ICI Pakistan has annual production capacity of 350,000 tons while Olympia Chemicals Ltd. has 165,000 tons. These industries produce the soda ash in quantity which is sufficient to meet the requirements of Pakistan; the rest is exported to other countries. For every ton of soda ash formed, some 1.5-1.7 tons of calcium chloride is generated. About 0.8 million tons of calcium chloride is produced annually as byproduct while producing sodium carbonate by soda ash industries in Pakistan. That is either dumped to the open land sites or is discharged to water ways where it pollutes the aquatic environment.

1.4 Uses of Calcium Chloride

Calcium Chloride has following uses:

- As a deicing agent used for the melting of ice and snow from the roads
- As an additive to drilling mud and oil well completion fluids
- As a dehydrator for drying petroleum fractions
- As a desiccant for moisture proofing

The above uses are mostly related to cold weather countries, however for Pakistan the only use of calcium chloride is in petroleum drilling. So there is need to make some other useful compound which has better applications.

1.5 Utilization of Calcium Chloride

Several studies have been carried to utilize $CaCl_2$ discharged from the Solvay process. Some of which are briefly deliberated here.

1.5.1 Recovering Cl_2 gas from Calcium Chloride

Ueno et al. recovered the chlorine (Cl_2) gas from calcium chloride [5]. Calcium chloride was introduced into the heat resistant vessel which had inlet pipe and outlet pipe for the gas. Calcium chloride was heated to 1073 K or greater. Meanwhile the air was introduced into the vessel through inlet pipe which produced the fused salt of $CaCl_2$. The oxygen present in the vessel reacted with fused salt to produced chlorine (Cl_2) and calcium oxide (CaO). The Cl_2 gas thus produced was discharged from the gas outlet of the vessel. The reaction involved can be represented as;

$$\mathrm{CaCl_2 + \frac{1}{2}O_2 \rightarrow CaO + Cl_2} \text{..1.10}$$

The above reaction is an endothermic reaction having an equilibrium constant (K_{eq}) of about 6×10^{-6} even at 1100K which is very small. So the temperature for equilibrium constant is higher than melting point (762 ^{o}C) of the $CaCl_2$. Thermodynamically the reaction between $CaCl_2$ and oxygen is very slow. This can be increased to a certain limit by removing the Cl_2 gas from the vessel as soon as it is formed.

Recovering the chlorine gas from the calcium chloride is not attractive as the cost of producing the heat for attaining desired temperature is so much high. Also Cl_2 is produced as co-product while producing sodium hydroxide (NaOH) which is cheaper source for production of Cl_2.

1.5.2 Synthesis of Calcium Hydrogen Phosphate

Mikhail Shiryaev et al. [6] synthesized the calcium hydrogen phosphate dihydrate ($CaHPO_4.2H_2O$) from the calcium chloride by reacting it with the potassium hydrogen phosphate (K_2HPO_4). The solutions of both $CaCl_2$ and K_2HPO_4 were mixed at 20 ^oC while stirring vigorously. Then the precipitate was filtered and dried. DE WAAL et al. also prepared the calcium hydrogen phosphate from calcium chloride. Calcium chloride and water were mixed and raised its temperature to about 1000 to 1200 ^oC and then it was put to the cyclone. After treatment in cyclone, calcium oxide (CaO) and hydrochloric acid (HCI) were formed. The CaO formed was reacted with phosphoric acid (H_3PO_4) to form calcium hydrogen phosphate.

In first case the price of potassium phosphate (K_2HPO_4) is much high which make the process uneconomical to make calcium hydrogen phosphate by the reaction of K_2HPO_4 and $CaCl_2$. In second case the temperature requirement is so high that to produce such temperature the cost of process increases from the cost of product formed which make the process uneconomical.

1.5.3 Production of Calcium metal by Electrolysis of $CaCl_2$

J. J. Lukasko et al. and Yurii P. Zaikov et al. [7, 8] produced the calcium metal by electrolysis of calcium chloride. $CaCl_2$-KCl in molten form was used as electrolyte in the electrolytic cell. The process consists of two steps (1) extraction of calcium metal at temperature of 650 to 715 ^oC at copper-calcium cathode by the electrolysis of $CaCl_2$-KCl in molten form and (2) then by using vacuum distillation for separation of calcium from the calcium rich alloy [9]. The whole process was continuous.

Although electrolytic method has high yield (70-80%) and purity of the product is also greater (99%) but the major drawbacks are, large power consumption, many reagents are used and electro winning calcium is multistage process and is also environmentally unsafe. To overcome these problems metallothermal process was adopted for the production of calcium metal. In this process calcium metal is obtained by reducing its oxide form (CaO). It is more flexible, consumes less power and is also less dangerous for environment. Although the product produced by metallothermal process is less pure than electrolytic process but it doesn’t matter as major use of calcium is in steel industry which doesn’t require the greater purity and main cause for implementation of metallothermal process is the economy. Cost of producing one ton of calcium metal is less as compared to electrolytic method.

1.5.4 Synthesis of Calcium Sulfate Whiskers from Calcium Chloride

Calcium sulfate whiskers are attractive to synthesize from the calcium chloride due to cost effectiveness and moderate process conditions. The other reagent involved in the reaction is very cheap which make the process economical. Investigators have used the calcium chloride as a starting material for the synthesis of calcium sulfate whiskers. A brief review is given below.

Xingfu Song et al. [10] prepared the calcium sulfate whiskers by reactive crystallization using sulfuric acid and calcium chloride discharged from the Solvay process. They studied the effect of various parameters like reaction temperature, reaction time and reactants concentration and optimized the conditions and then successfully prepared the calcium sulfate whiskers with high aspect ratio. Huazi Xu et al. used calcium chloride to synthesize calcium sulfate hemihydrate (CSH) by the salt solution method [11]. Baohong Guan et al. developed the CSH in the calcium chloride solution containing K^+ and Mg^{2+} at high temperature [12]. Thomas Feldmann et al. carried out the growth of CSH in $CalCl_2$-HCl solution media by using salt solution method [13]. Jingwei Mao et al. prepared the calcium sulfate starting from calcium chloride and potassium chloride by salt solution method [14]. Kangbi Luo et al. prepared the calcium sulfate whiskers by reacting the calcium chloride and sodium sulfate by hydrothermal process [15]. Qing Han et al. synthesized the CSWs from calcium chloride and potassium sulfate by hydrothermal method [16].

Calcium sulfate whiskers have wide range of applications. They are used as filler material in rubber, plastics, paper making and cement. Calcium sulfate whiskers being thermally stable, resistant to chemicals, exhibit excellent compatibility with plastics. Calcium chloride is cheap raw material for the production of calcium sulfate whiskers. CSWs manufactured from calcium chloride are cost effective and have large aspect ratio that makes them suitable for use as reinforcing material in polymer composites. Moreover the price of calcium sulfate whiskers is also small as compared to other inorganic whiskers e.g. silicon carbide [17, 18].

1.6 Organization of Thesis

Chapter-1 (Introduction)

Solvay process, Solid waste from Solvay process, Soda ash industry in Pakistan, Utilization of calcium chloride into chemical products

Chapter-2 (Literature Review)

Inorganic whiskers, Calcium sulfate whiskers, Raw materials for calcium sulfate whiskers, Objectives

Chapter-3 (Review on Experimentation and Characterization)

Different methods for synthesis of calcium sulfate whiskers, Characterization techniques i.e. SEM, XRD, UTM for CSWs

Chapter-4 (Experimentation)

Synthesis of CSWs, Process parametric study, PCL-CSWs composite formation

Chapter-5 (Results and Discussion)

Optimization of process parameters i.e. temperature, molar ratio of reactants, mixing ways of reactants. Additives effect on CSWs, Enhancement of mechanical strength of PCL-CSWs composite

Summary

Solvay process is synthetic process, used for the production of sodium carbonate. Sodium carbonate is important raw material for production of glass, pulp & paper, soap & detergents and many other industrial products. Calcium chloride is produced as byproduct during the production of sodium carbonate. Calcium chloride is discharged to the water ways or open land sites where it causes environmental hazards. Calcium chloride can be used to produce calcium metal, calcium hydrogen phosphates and chlorine gas. But in these processes large amount of energy is required which make the processes infeasible. Synthesis of calcium sulfate whiskers from calcium chloride is attractive due to cost effectiveness and moderate process conditions.

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Chapter 2

Literature Review

2.1 Inorganic Whiskers

Whiskers are short fiber-shaped distinct crystals having high aspect ratio. Aspect ratio is length to diameter ratio (L/D ratio) that is used to characterize the whiskers. High strength, stiffness and reduced internal defects such as dislocations due to small diameter, make the whiskers excellent reinforcing material that has attracted the interests of engineers and scientists over the past ten years [1-4]. Compared to traditional carbon and glass fibers which have short length and are expensive to produce, inorganic whiskers having high specific strength are more effective strengthening materials. Significant development has been made in the synthesis of inorganic whiskers and their applications in the composite materials during the last decade.

Composite materials can be strengthened by several potential inorganic whiskers which include potassium titanate ($K_2Ti_6O_{13}$) [2], silicon carbide (SiC) [5], calcium carbonate ($CaCO_3$) [6], aluminum borate ($Al_{18}B_4O_{13}$) [7] and calcium sulfate ($CaSO_4.0.5H_2O$) [8]. However, some inorganic whiskers like SiC and $Al_{18}B_4O_{13}$ are harmful for human beings and are also expensive to yield which limit their applications in composite materials [9]. Calcium sulfate whiskers compared to the other inorganic whiskers, are environment friendly, cost effective and have slight toxicity. They are of merely 1/200 ~ 1/300 to the price of SiC whiskers [8, 10]. Some of the particular features of calcium sulfate whiskers are as follows;

- Exhibit good compatibility with rubber, plastic and polymers.
- Thermally stable and resistant to chemicals.
- Have good reproducibility.
- Have excellent mechanical properties like high tensile strength, high modulus of elasticity.

2.2 Calcium Sulfate Whiskers

Calcium sulfate has a total of six forms which are known, of which three forms precipitates naturally and in different industrial processes which include calcium sulfate dihydrate ($CaSO_4.2H_2O$), calcium sulfate hemihydrate ($CaSO_4.0.5H_2O$) and anhydrous calcium sulfate ($CaSO_4$). Calcium sulfate in hemihydrate form are called calcium sulfate whiskers. Due to wide range of applications in rubber, plastics, paper making, ceramics and friction materials, many researchers have focused on the preparation of calcium sulfate whiskers from different materials and by using different methods mainly to reduce their cost.

2.3 Raw materials for Calcium Sulfate Whiskers

2.3.1 Commercial Grade Gypsum

It is chemically known as calcium sulfate dihydrate. It occurs in sedimentary rock formation. It is mined in rock form, crushed and then ground to fine powder. It is calcined at temperature of 150-175 ^{o}C to convert it into hemihydrate form. Gypsum quarried from rock contains some impurities e.g. calcite ($CaCO_3$), pyrite (FeS_2), halite (NaCl) and sulfur (S) [11, 12].

S.C. Hou et al. synthesized the calcium sulfate whiskers by facile calcination-hydration hydrothermal method from the commercial grade gypsum. The gypsum was first converted into active form by calcination at 150 ^{o}C for 6 h and then hydrothermal treatment was done to transform $CaSO_4{\cdot}2H_2O$ into $CaSO_4{\cdot}0.5H_2O$ whiskers. The whiskers so produced had a length of 30-200 µm and diameter of 0.1-0.5 µm [13].

2.3.2 Flue Gas Desulfurization (FGD) Gypsum

FGD gypsum is produced during wet flue gas desulfurization processes. In these processes calcium based absorbents are used for scrubbing the flue gases from coal power plants. Flue gas desulfurization processes are dominant among the other processes for scrubbing flue gases because of their reliability, cost effectiveness and higher efficiency for removing SO_2 [14]. In flue gas desulfurization processes, FGD gypsum is produced as byproduct in large quantities which is problematic for environment. So scientists have made efforts to utilize FGD gypsum both technically and economically.

YANG LiuChun et al. and Baohong Guan et al. prepared the calcium sulfate whiskers from FGD gypsum by using salt solution method. They found that CSH can be synthesized under mild conditions (at temperature of 95 ^{o}C and under atmospheric pressure) but morphology of the CSH is affected by the reaction conditions i.e. pH and additives [14, 15]. Xiao Wang et al. synthesized the calcium sulfate whiskers from FGD gypsum in H_2SO_4-NaCl-H_2O system by hydrothermal crystallization. They examined the morphology of calcium sulfate whiskers precipitated out of NaCl-H_2O, H_2SO_4-H_2O and H_2SO_4-NaCl-H_2O system. H_2SO_4-NaCl-H_2O system was found to be best for the growth of CSWs. The whiskers formed in this system had length of 200 to 600 µm and diameter of 3 to 5 µm. The phase structure of whiskers was hemihydrate [16].

Baohong Guan et al. manufactured the calcium sulfate hemihydrate from FGD gypsum in recycling mixed salt solutions. The effects of salt solution recycling on the formation and quality of CSH were investigated. Results revealed that FGD gypsum can be converted to CSH in recycled salt solution media in 3.5 – 6 h. The CSH formed was 95% pure and had good morphology [17]. Ai-Ye Xu et al. prepared the calcium sulfate whiskers from desulfurization gypsum containing $CaCO_3$. Desulfurization gypsum consist of $CaSO_4{\cdot}2H_2O$ (93%) and remaining CaCO3. The $CaCO_3$ present in the desulfurization gypsum was converted to gypsum by calcination-acidification and then hydrothermal treatment of purified gypsum was carried out to convert them into calcium sulfate whiskers. The whisker produced in this method had length of 200-400 µm and the diameter of 1-5 µm [18].

2.3.3 Phosphogypsum (PG)

Phosphogypsum is produced as a byproduct during the production of phosphoric acid. PG mainly contains calcium sulfate dihydrate and some impurities e.g. phosphates, fluorides and silica. Huge masses of PG, approximately 150 million tons are produced in the world each year and only 4.5% is used, the rest is discarded [19]. Therefore many scientists have put their efforts to utilize this byproduct.

Ma Baoguo et al. synthesized the CSH from phosphogypsum (PG) in calcium chloride solution under atmospheric conditions by slat solution method. The effects of temperature and $CaCl_2$ solution percentage for the development of CSH were studied. The optimum temperature found was 95 ^{o}C and 24 wt. % $CaCl_2$ solution to the phosphogypsum [20]. Hua He et al. prepared the CSH by hydrothermal method starting from phosphogypsum and studied the influence of glycerol on preparation of CSH. Glycerol/water volume ratio of 50% was found to be ideal. The whiskers so formed had an average length of 38 - 85 µm, diameter of 0.7-1.3 µm and aspect ratio of 29-118. The whiskers had also high yield of about 89-96% [21].

HUANG Zheyuan et al. PG as a starting material for the preparation of calcium sulfate whiskers by hydrothermal method. Optimum conditions investigated were reaction time of 2 h, reaction temperature of 140 ^{o}C, and solid/liquid ratio of 1:10. Glycerin was found to be best additive having optimal volume ratio, Vol of glycerin/ Vol of soln. = 50%. The whiskers so formed had diameter of 1-3 µm and aspect ratio of 45. The yield came out to be 95 % [22].

2.3.4 Calcium oxide (CaO) and sulfuric acid

Yuanbing Ling et al. prepared the CSH by reaction of calcium oxide (CaO) with sulfuric acid under atmospheric conditions. They found the optimum conditions for the preparation of CSH comprising sulfuric acid concentrations of 0.6-1.1 M, molar ratio of CaO/H_2SO_4 to be 0.4, temperature of 98-105 ^{o}C, and residence time of 1 h. CSH so produced had length of 50-100 µm and diameter of 1-3 µm [23]. Zongyou Pan et al. prepared the CSH from sulfuric acid and calcium hydroxide $Ca(OH)_2$ by hydrothermal method and studied the effects of ethanol on the morphology of CSH. By the addition of ethanol, water activity diminished in the reaction mixture. The CSH formed had unvarying size and morphology [24].

2.3.5 Calcium Chloride

Huazi Xu et al. used calcium chloride to synthesize calcium sulfate hemihydrate (CSH) by the salt solution method. The effect of pH and succinic acid were studied as an additive on the morphology of CSH. The optimized conditions for the conversion of CSD to CSH were pH in between 1.50 and 3.00 in presence of succinic acid while in the absence of succinic acid pH was less than 10.00. The ionized succinic acid delivered carboxyl group that altered the crystal development [25].

Xingfu Song et al. used calcium chloride and sulfuric acid for the production of calcium sulfate whiskers by reactive crystallization. Optimized conditions found were reaction time of 120 min, reaction temperature of 102 ^{o}C, and reactant’s concentration of 1 mol/L. The whiskers so formed had an average diameter of 4.73µm and aspect ratio of 191 [26].

Baohong Guan et al. developed the CSH in the calcium chloride solution containing K^+ and Mg^{2+} at high temperature. The effects of K^+ and Mg^{2+} ions were investigated. Results revealed that 3.74M solution is necessary for the growth of CSH at 80-100 ^oC whether K and Mg ions are present or absent. Both K^+ and Mg^{2+} ions have accelerating effect on the growth of CSH [27].

Thomas Feldmann et al. carried out the growth of CSH in $CalCl_2$-HCl solution media by using salt solution method and adapting semi batch process. They examined the effects of flow rate of reactants, reaction temperature and input power for stirring. The optimum flow rate was 0.3 mol per hour while temperature and input power had not obvious effect on the growth of CSH [28].

Jingwei Mao et al. synthesized the calcium sulfates from calcium chloride and potassium chloride by salt solution method and studied the reliance of metastable life time (MLT) at temperature (25-95 ^oC) and citric acid having concentrations of 0.1-1.0mM. Calcium sulfates has metastable form known as hemihydrate (HH). MLT of HH was short while converting to dihydrate (DH) and was long for anhydrate (AH). At temperature of 45-75 ^oC citric acid stimulated the expansion of MLT [29].

Qing Han et al. synthesized the CWS from calcium chloride and sodium sulfate by hydrothermal method and examined the effect of disodium-hydrogen phosphate dodecahydrate ($Na_2HPO_4.12H_2O$) on the formation of CSW. The addition of $Na_2HPO_4.12H_2O$ enhanced the conversion of calcium sulfate dihydrate to calcium sulfate hemihydrate and reduced the whiskers in dimensions i.e. length and diameter. The whiskers so produced had length of 20-200 µm and diameter of 0.5 – 2 µm. The aspect ratio also reduced by the addition of $Na_2HPO_4.12H_2O$ in solution [30].

2.3.6 Carbide Slag

Carbide slag is the discharged waste in the production of acetylene from calcium carbide and water. Carbide slag chiefly consists of calcium hydroxide. This calcium hydroxide can be used to produce calcium based materials.

Yongqian Wang et al. prepared the calcium sulfate whiskers from carbide slag by hydrothermal method. The effects of reaction parameters like reaction temperature, reaction time, seriflux concentration and seriflux pH were investigated on the morphology of CSWs. Prime conditions found were, reaction temperature of 130 ^oC, reaction time of 10 h, seriflux concentration of 4 % and pH of 7. The aspect ratio of the whiskers formed was 60 to 80 µm [31].

Jen-Chang Yang et al. developed a direct method for the preparation of calcium sulfate hemihydrate by mixing K_2SO_4 and $Ca(NO_3)_2.4H_2O$ in $CaCl_2$ solution. Calcium sulfate dihydrate formed as transitional product that converted to calcium sulfate hemihydrate. The conversion of CHD to CSH accelerated by increasing the concentration of $CaCl_2$ solution. Reaction temperature and molar ratio of $CaCl_2$ in solution were two key factors, controlling the phase of calcium sulfate [32].

2.4 Objectives

In context of the detailed discussion in the first two chapters of this thesis and after a detailed literature review the objectives of current study are defined as follows:

- Synthesis of calcium sulfate whiskers (CSWs) from calcium chloride discharged from Solvay process by hydrothermal method.
- To study the effects of process parameters (temperature, mixing ways of reactants and molar ratio of reactants) on morphology and aspect ratio of CSWs.
- To study the effects of additives on the formation and aspect ratio of CSWs.
- Synthesis of CSWs/polycaprolactone (CSWs-PCL) composite by co-precipitation method.
- Use of CSWs in PCL for improvement in mechanical properties of PCL-CSWs composite.

Summary

Whiskers are short fiber-shaped distinct crystals having high aspect ratio. Calcium sulfate whiskers compared to the other inorganic whiskers, are environment friendly, cost effective and have slight toxicity. Calcium sulfate has total of six forms of which three forms i.e. calcium sulfate dihydrate, calcium sulfate hemihydrate and calcium sulfate anhydrate precipitate naturally. Calcium sulfate in hemihydrate form are called calcium sulfate whiskers. CSWs can be prepared from different materials which include commercial grade gypsum, flue gas desulfurization (FGD) gypsum, phosphogypsum (PG), calcium oxide (CaO) and sulfuric acid, calcium chloride, carbide slag and potassium sulfate and calcium nitrate in $CaCl_2$ solution for the production of calcium sulfate whiskers. Calcium chloride being cheap, easily available and impurity free chemical is most suitable for the synthesis of calcium sulfate whiskers. At the end of this chapter, the objectives of this study are given to carry out the detailed experimentation.

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Chapter 3

Review on Experimentation and Characterization Techniques

In this chapter a brief review about the different methods for the synthesis of calcium sulfate whiskers is given along with characterization techniques which are normally used for analysis of CSWs.

3.1 Methods for the preparation of Calcium Sulfate Whiskers

Following methods have been used for the production of calcium sulfate hemihydrate whiskers.

3.1.1 Hydrothermal Method

In this method, firstly calcium sulfate dihydrate ($CaSO_4.2H_2O$) are formed either from gypsum directly or by reacting the reagents containing calcium and sulfates to form calcium sulfate dihydrate and then hydrothermal treatment is performed under steam pressure of about (20-40 psi or 138-276 kPa) and at temperature of 150 ^{o}C for 4 - 6 h. The reaction describing the hydrothermal method is given by equation 1.

$$CaSO_4.2H_2O \rightarrow CaSO_4.0.5H_2O + 1.5H_2O .... 3.1$$

The operating conditions may vary slightly as described above. However the complete conversion from calcium sulfate dihydrate to calcium sulfate hemihydrate can be achieved at steam pressure of 25.7 psi for 7 h and at 36 psi for 4 - 6 h as reported by Singh and Rai [1]. Industrially the most successful process in practice is SICOWA-ProMineral hydrothermal/autoclaving from Germany [2].

3.1.2 Oxidation Method

The SO_2 in gaseous form is reacted with calcium hydroxide $Ca(OH)_2$, commonly known as slaked lime and the slurry so formed is then oxidized to hemihydrate in pressurized vessel at 100-145 ^{o}C and under pressure of 20-60 psi (138 - 414 kPa). This process is recognized by Omega process and was developed in the USA [3].

Other processes for the manufacture of calcium sulfate hemihydrate in the literature are reported in which curing of calcium sulfate dihydrate is involved in different salt solutions or acid solutions [4, 5] but they are not being used on commercial scale. Brief description of these processes is as follows;

3.1.3 Salt solution method

The general procedure of the method is as follows. In this method batch reactor is used that is equipped with reflux condenser for vapor reflux and a Teflon stirrer for obtaining homogenous suspension. The temperature of the reactor is monitored by thermometer. Temperature has normal range of 110 to 120 ^{o}C. In a typical synthesis 30 wt. % calcium chloride solutions with various reaction mediums are used for the synthesis of calcium sulfate hemihydrate. The solution is constantly stirred for half an hour to obtain uniform suspension. Then the solution is transferred to another flask that is preheated to certain temperature with stirring. In flask calcium sulfate dihydrate powder is added and reacted for about 48 hours. After that the slurry is filtered and dried at 110 ^{o}C for 30 minutes in an oven [6-10]. The resultant product is calcium sulfate hemihydrate. The whole procedure can be abridged into two steps; in the first step dissolution of calcium sulfate dihydrate (CSD) occurs while in the second step calcium sulfate hemihydrate (CSH) precipitates.

3.1.4 Microemmulsion method

Briefly in the microemmulsion method, two reactants (say A and B) are introduced in two identical microemmulsion. Upon mixing of two reactants, the droplets collide and exchange the reactants. The small droplets serve as micro reactors where the reaction takes place. Many variations in this procedure have been employed. For instance, one of the reactants can be placed in the solution into the microemmulsion containing the other reactant or can be added directly to microemmulsion as solid, liquid or gas. Use of two identical microemmulsion containing reactants is commonly used method for chemical synthesis. Bao Kong et al. established a reverse microemmulsion method of water n-hexanol for the synthesis of α-calcium sulfate hemihydrate submicron rods. They designated the water/n-hexanol/cetyltrimethylammonium bromide (CTAB) system and synthesis reactions were carried out at temperature of 80-95 ^{o}C. Lower temperature (80

^{o}C) favored the formation of dihydrate while hemihydrates were formed higher temperature (95 ^{o}C) [11, 12].

3.1.5 Organic-water system

The overall procedure is as follows: extractant N1923 is used as primary ammine. The SO_4^{2-} ions are extracted from the primary amine in organic phase while Ca^{2+} are extracted into organic solvent by another ammine, bis(ethylhexyl) hydrogen phosphate (HDEHP). $Ca(DEHP)_2$ is prepared by mixing $Ca(NO_3)_2$ aqueous solution with HDEHP heptane in a suitable quantity. The pH of aqueous phase is adjusted to 6 by ammonia solution. After reaching at equilibrium stage the organic phase is separated and used in the experiments.

For preparation of primary ammine sulfate, the extractant (primary amine) is dissolved in sulfuric acid solution so that it converts to primary amine sulfate. After the equilibrium is developed between organic phase and aqueous phase, the organic phase is separated for use in the following experiments. Calcium sulfate crystals are formed by mixing equal volumes of primary amine sulfate in n-heptane and $Ca(DEHP)_2$ organic solution. The precipitates formed are filtered, washed with absolute ethanol [13]. The product formed is calcium sulfate hemihydrate.

3.1.6 Microwave assisted method

Liang Li et al. reported a microwave assisted route for the preparation of calcium sulfate hemihydrate nanowires by using calcium dodecyl sulfate (CSD) as a precursors. Calcium dodecyl sulfate was prepared by mixing $CaCl_2$ and saturated solution of sodium dodecyl sulfate (SDS). The precipitates formed were collected by centrifugation, washed with deionized water and dried in vacuum at 60 ^{o}C. Microwave oven was used for thermal transformation of calcium dodecyl sulfate to calcium sulfate hemihydrate. The slurry was stirred for 15 minutes while transformation to hemihydrate.

Research results revealed that microwave assisted method didn’t require any seed or template for the preparation of calcium sulfate hemihydrate. The different organic solvent had a little effect on the morphology of calcium sulfate HH. Microwave heating also reduced the reaction time for the synthesis of calcium sulfate hemihydrate nanowires as compared to oil heating method [14].

3.1.7 Ultrasound-Assisted Method

Chinmay Hazra et al. disclose the ultrasound assisted/bio surfactant templated route for the synthesis of calcium sulfate α-hemihydrate with controllable morphology.

The overall procedure is as follows; the anionic biosurfactants i.e. rhamnolipids and surfactin were isolated and purified from Pseudomonas aeruginosa and Bacillus claussi respectively, as reported in literature [15, 16]. For the synthesis process 100ml beaker was used with constant rate of 250 rpm. The temperature of the solution was kept constant at ambient temperature. In situ deposition technique was used for the synthesis of nanosized $CaSO_4$. Briefly, $CaCl_2$ (0.1M) was added into 100 ml distilled water. For experimentation the biosurfactants was transferred into the calcium solution before mixing with the sulfate solution. Biosurfactants was added in variable quantity in the aqueous calcium solution having a rhamnolipid/H_2O or surfactin/H_2O mass ratio ranging from 1.3 - 4.5 (step 1 solution). Aqueous calcium solution containing biosurfactants was exposed to irradiation for 10 min then it was transferred to the ultrasonic reactor. Another solution of $(NH_4)_2SO_4$ (0.1M) was put into step 1 solution and ultrasound irradiation was generated with a high intensity ultrasonic processor for 1 h to procedure $CaSO_4$ particles. During sonication the temperature was kept constant at 30 ^oC by using ice bath so the external temperature had no effect on the reaction. The solid product obtained was washed with distilled water four times, rinsed with acetone and dried at 60 ^oC for 2 hours.

From the above methods described, only two methods i.e. hydrothermal and oxidation method are proven technologies for the commercial production of calcium sulfate whiskers. The other methods are just used in laboratory as the technology is not mature for these methods to apply for production of CSWs on the commercial scale.

3.2 Characterization Techniques

3.2.1 X-ray Diffraction (XRD)

X-rays are electromagnetic radiation having a wavelength of about 1 Å. These are used for the phase identification and structural arrangement of atoms and molecules in wide range of materials because their wavelength is almost same as the size of an atom. X-rays are generated when a high energy electron beam is accelerated through a high voltage field, typically ranging from 50 –150 kV provided by the x-ray generator, bombards on solid metal target normally tungsten or molybdenum. As incident electrons collide with atoms in the target, the inner shell electrons in atoms will be ejected through ionization process by the high energy electrons. A free electron in an outer orbital will immediately fill the vacant site and an X-ray photon is emitted due to the energy released in the transition. The relationship between the energy 'E' of X-ray radiations and its wavelength is given by the equation 2. Where h is Planck's constant, c is the speed of light in vacuum and λ is the characteristic wave length.

$$E = \frac{hc}{\lambda} \qquad \text{........3.2}$$

After the collision of X-rays with the crystals, some of them will be deflected away from the direction they originally travel and these deflected X-rays are measured in diffraction experiments. The scattered X-rays carry information about the electron distribution in materials and each crystalline solid has its unique X-ray pattern, therefore it can be used as a 'fingerprint' for identification.

Bragg's law describes x-ray diffraction by relating the wavelength of electromagnetic radiation with diffraction angle and lattice spacing of crystalline sample. The derivation of Bragg's Law is shown in Figure **3.1**. The incident beams are always in phase and parallel up to the points A&D, where beam 1 strikes the top layer at atom D, while beam 2 continues to the next layer where it is scattered by atom B. Therefore, beam 2 must travel an extra distance (AB + BC) before the two beams continue to travel adjacent and parallel as 1'& 2'. This extra distance must equal an integral (n) multiple of the wavelength (λ) for the two beams to be in phase.

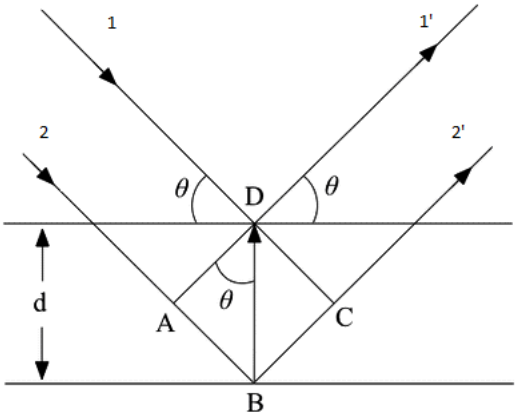

Figure 3.1. Bragg's law description

‘d’ is the perpendicular distance between pairs of adjacent planes and θ is the angle of incidence, therefore:

$$AB = BC = d\text{Sin}\,\theta$$

$$2AB = n\lambda$$

$$2d\text{Sin}\,\theta = n\lambda \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.3$$

Constructive interference of the radiation reflected from the plane of crystal occurs when the path difference is an integral multiple of wavelength λ as given by equation 3. When n is integral (1, 2, 3) the reflected rays from the different layers are impeccably in phase with each other and produce a bright point on the photographic film on the other hand when ‘n’ in not integral the image will not be produced on the photographic film. The unknown sample is scanned through a range of 2θ angles and in this way all the probable diffraction trend of the lattice can be attained. The identification of the mineral is carried out by conversion of the peaks to d-spacing as each mineral has a specific d-spacing. The d-spacing obtained from the sample are compared with standard reference pattern [17, 18].

3.2.1.1 Applications

X-ray powder diffraction is broadly used technique for the identification of unfamiliar crystalline materials e.g. minerals and inorganic compounds. Determination of unknown compound is very important in research and engineering. Other applications of X-ray powder diffraction comprise;

- Characterization of crystalline materials
- Determination of unit cell dimensions
- Measurement of sample purity

3.2.1.2 Strengths and Limitations of X-ray Powder Diffraction

Following are the strengths of XRD;

- Powerful and rapid (< 20 min) technique for identification of an unknown mineral
- In most cases, it provides an unambiguous mineral determination

- Minimal sample preparation is required
- Data interpretation is relatively straight forward
- Identification of compounds not just elements

Limitations of XRD are as follows;

- Not stand alone technique, require chemical data for identification
- Must have access to a standard reference file of inorganic compounds
- Requires tenths of a gram of material which must be ground into a powder

3.2.2 Scanning Electron Microscopy (SEM)

The electron microscope uses a beam of electrons to create an image of the specimen. It is capable of much higher magnifications and has a greater resolving power than a light microscope as the wavelength of electron is 100,000 times smaller than visible light, allowing it to see much smaller objects in finer detail.

A Scanning Electron Microscope (SEM) takes images by scanning across a rectangular area of the sample with a focused electron beam. Particularly, an electron gun is used for the thermionic emission of the electron beam. This electron gun is fitted with a tungsten filament cathode. Tungsten is used for heating in thermionic electron guns to produce an electron beam because of its highest melting point and lowest vapor pressure among metals. The electron beams are focused by several condenser lenses to a spot with ~ 4–50 Å diameters and are adjusted and controlled by the deflection coils before finally incident onto the sample. The electrons lose energy when the electron beam interacts with the specimen and the lost energy will be converted into other forms such as heat, emission of secondary electrons and emission of light or X-rays, which can be detected by specialized detectors. Figure 3.2 shows a schematic diagram of a SEM [19].

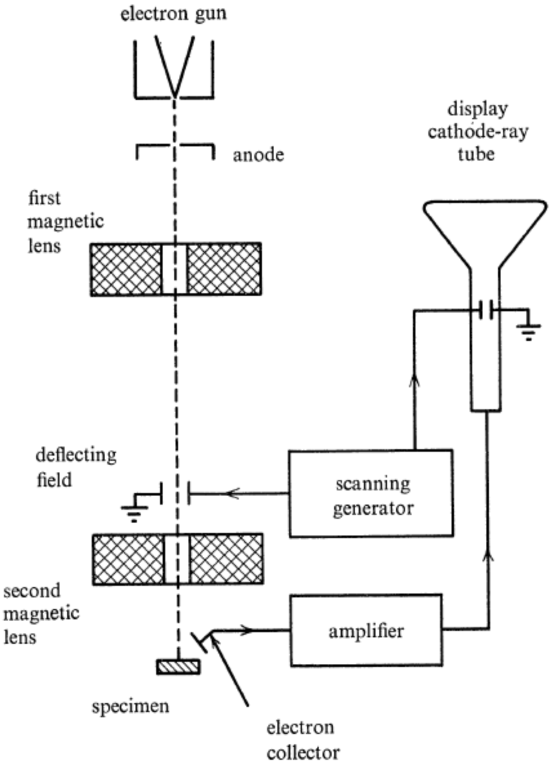

Figure 3.2. Schematic demonstration of SEM

3.2.3 Universal Testing Machine

Universal testing machine (UTM) is called so because of its versatile applications for material testing. To study the mechanical properties of the materials following tests can be executed with UTM.

- Tensile test
- Compressive test
- Bending test
- Hardness test

3.2.3.1 Principle of Operation

Operation of the machine is based on hydraulically transmitting the load from the test specimen to a distinctly held load indicator. Load is applied by hydrostatically lubricated ram. Main cylinder pressure is transmitted to the pressure transducer which is contained in the control panel. The signal from the transducer is given to electronic display unit, equivalent to the load employed by the main ram. Immediately the digital encoder gives the mechanical displacement which is fitted on the straining unit. Figure **3.3** shows the schematic of universal testing machine [20].

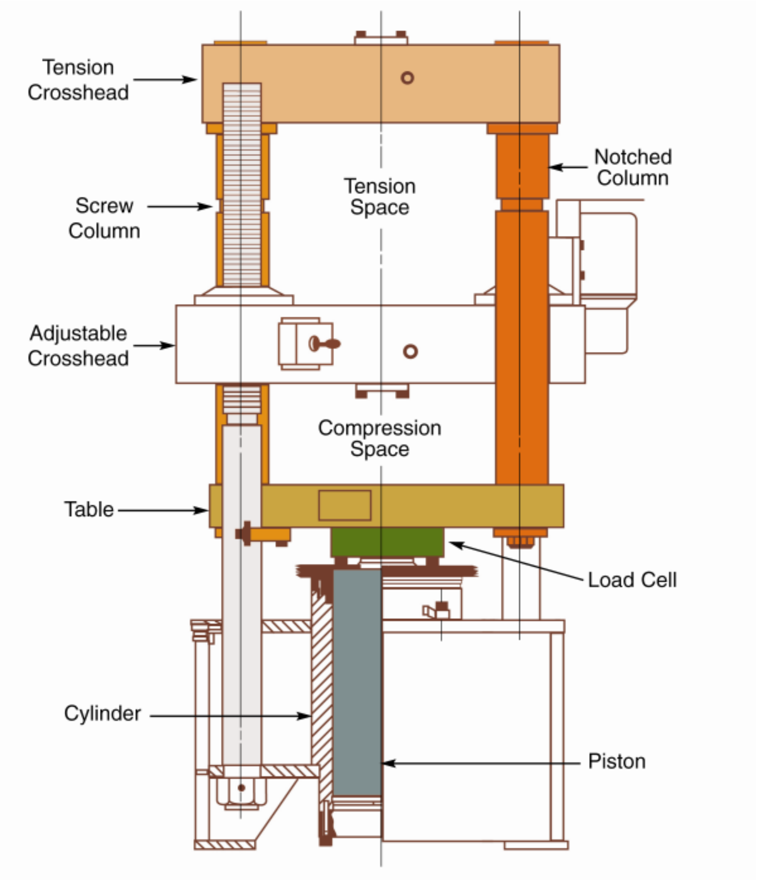

Figure 3.3 Schematic of single acting universal testing machine (UTM)

3.2.3.2 Main units of Universal Testing Machine

- **Straining unit**

This consists of cylinder motor with a chain & sprocket drive and a table coupled with ram of hydraulic cylinder, mounted on a robust cylinder.

- **Control panel**

It consist of power pack complete with drive motor, control valves and electronic display unit.

- **Power pack**

It generates maximum pressure which varies according to the capacity of the machine. The hydraulic pump provides flow of oil for load application.

Summary

In this chapter a brief review of different experimental has given for synthesis of calcium sulfate whisker. Two methods namely hydrothermal and oxidation methods are in practice for the commercial production of calcium sulfate whiskers. Both methods are having mature technology. However, hydrothermal method is more suitable for the synthesis of calcium sulfate whiskers due to flexibility of raw material and easily controllable reaction conditions. Other methods which includes salt solution method, microemmulsion method, organic-water system, microwave assisted method and ultrasound-assisted method are also used for the synthesis of calcium sulfate whiskers. These methods are only being used in laboratory. In the second part of chapter characterization techniques were described that are uses for analysis of CSWs. Characterization techniques like X-ray diffraction and scanning electron microscopy are used for the phase determination and microstructure analysis of compounds. Electronic universal testing machine is used for the study of mechanical properties of PCL-CSWs composites.

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Chapter 4

Experimentation

A series of experiments were performed to achieve the specific objectives defined in the 2nd chapter of thesis. However, the details of major experiments are given in this chapter:

- Synthesis of calcium sulfate dihydrate (CSD) precursors at various temperatures to study the effects of temperature on the morphology and aspect ratio of corresponding hydrothermal product which are calcium sulfate hemihydrate (CSH), also known as calcium sulfate whiskers.
- Synthesis of calcium sulfate whiskers with different mixing ways of reactants.
- Synthesis of calcium sulfate whiskers by adding the reactants with different molar ratio to study the effects of reactant's concentrations on the morphology and aspect ratio of calcium sulfate whiskers.
- Synthesis of calcium sulfate whiskers in the presence of additives.
- Synthesis of calcium sulfate whiskers-polycaprolactone composites to improve the strength of the composite material.

4.1 Materials

Sodium sulfate (Na_2SO_4) (Cat. No.746363), calcium carbonates ($CaCO_3$) (Cat. No.C6763) and polycaprolactone ($(C_6H_8O_2)_n$) (Cat. No.704105) of the analytical grade were purchased from Sigma-Aldrich Ltd. Polycaprolactone had an average molecular weight of 45,000. Calcium chloride ($CaCl_2$) was collected from the sodium carbonate production plant "ICI Soda Ash" located in Kherwa, district Chakwal, Pakistan.

4.2 Equipment

4.2.1 Hydrothermal Reactor

Hydrothermal autoclave was used as a reactor for the hydrothermal treatment of precursors formed by precipitation of calcium chloride and sodium sulfate. Its shell consisted of stainless steel while the inner lining was made-up of polytetrafluoroethylene (PTFE) as is shown in Figure 4.1 The reactor had heating and cooling rate of ≤ 5°C min^{-1} and can be operated at temperature of ≤ 260 °C and pressure of ≤ 2 MPa [1].

Figure 4.1 Hydrothermal synthesis autoclave reactor with PTFE lined

4.2.2 Oven

Temperature control is an imperative for the hydrothermal synthesis of whiskers as the conversion between calcium sulfate dihydrate and hemihydrate takes place at specific temperature. Oven (UNE-500 Memmert, Germany) with precise temperature control was used. Temperature rises with 3°C per min rate. The operating varies from 10 °C above ambient temperature to 300 °C. Heating system consists of a coat with natural air circulation [2].

4.3 Experimentation and Characterization of Calcium Sulfate Whiskers at various temperatures

4.3.1 Synthesis of Calcium Sulfate Whiskers at various temperatures

Calcium sulfate dihydrate were prepared by mixing Na_2SO_4 and $CaCl_2$ in solution form and in stoichiometric amounts at temperature of 25 °C, 55 °C and 85 °C to study the effects of temperature on morphology and aspect ratio of CSWs. The two solutions were mixed very slowly by keeping the dripping rate of 3mL.min^{-1}. The stirring speed was kept at (100-250 rpm). After mixing the raw materials, the suspension was stirred for 1-2 h. The precursors formed were then put into hydrothermal synthesis autoclave reactor to convert them into calcium sulfate hemihydrate. Hydrothermal autoclave reactor having an inner volume of 50ml, heated (3 °C.min^{-1}) to 130-150 °C and kept in isothermal conditions for 4.0-6.0 h. After that, the product was cooled down to room temperature naturally, filtered, washed with distilled water and dried at 105 °C for 2 h in oven. The resultant product was calcium sulfate whiskers. Figure **4.2** shows the synthesis scheme.

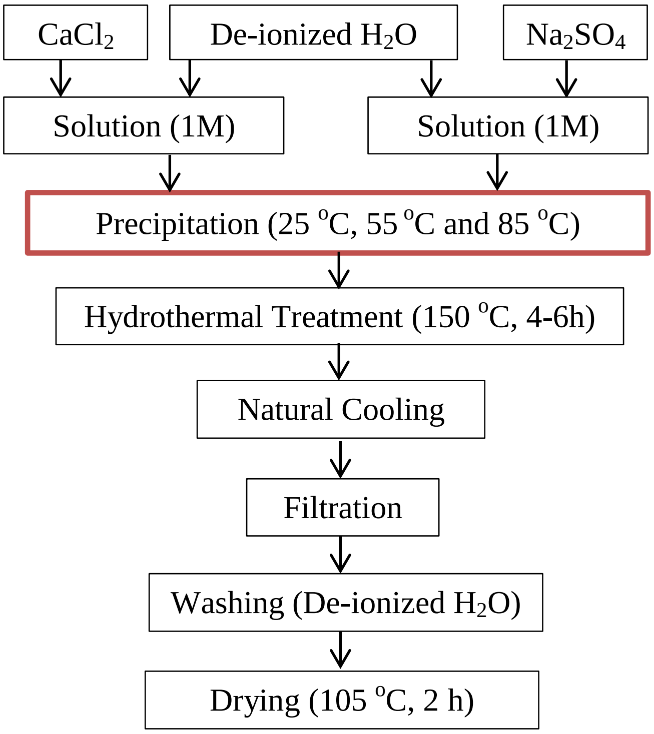

Figure 4.2 Flow chart for synthesis of CSW at temperatures (25 °C, 55 °C and 85 °C)

4.3.2 Characterization

Phase purity of the precursors, calcium sulfate dihydrate and hydrothermal product, calcium sulfate hemihydrate was determined by X-ray diffraction equipment (XRD STOE Germany). X-ray powder diffraction (XRD) of the sample was recorded using CuKα radiation ($\lambda = 1.5425$), with 2θ varying from 10° to 70°. The morphology and particle size of the synthesized samples were examined by scanning electron microscopy (FESEM, JSM-6490LA, JEOL, JAPAN).

4.4 Synthesis and characterization of Calcium Sulfate Whiskers with different mixing ways of reactants

4.4.1 Synthesis of Calcium Sulfate Whiskers with different mixing ways of reactants

Calcium sulfate dihydrate were synthesized by mixing Na_2SO_4 to $CaCl_2$ and vice versa in stoichiometric amounts and at temperature of 25 °C to study the effects of mixing ways on CSWs. In these experiments, the optimized temperature (25 °C) from the previous experiments was used. Two solutions were mixed very slowly by keeping the dripping rate of 3mL.min^{-1}. The stirring speed was kept at (100-250 rpm). After mixing the raw materials, the suspension was stirred for 1-2 h. The precursors formed were then put into a small stainless steel hydrothermal synthesis autoclave reactor to convert them into calcium sulfate hemihydrate. Hydrothermal reactor having an inner volume of 50ml, heated (3 $^{o}C.min^{-1}$) to 130-150 ^{o}C and kept in isothermal conditions for 4.0-6.0 h. After this, the product was cooled down to room temperature naturally, filtered, washed with distilled water and dried at 105 ^{o}C for 2 h in the oven. The resultant product was calcium sulfate whiskers. Figure 4.3 shows the major steps of process.

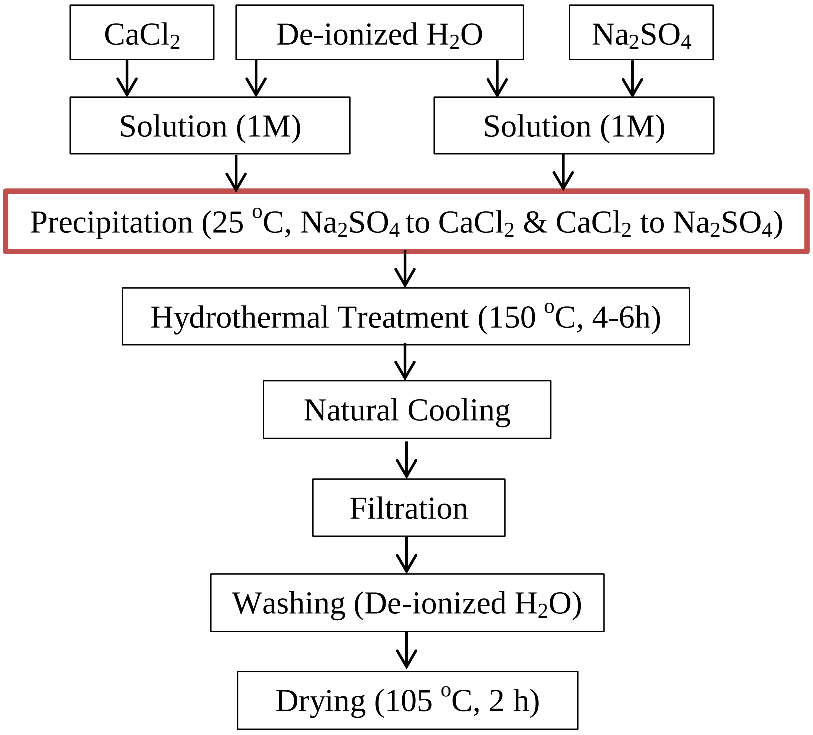

Figure 4.3 Flow chart for synthesis of CSW with different mixing ways of reactants

4.4.2 Characterization

The morphology and the particle size of samples formed were examined by scanning electron microscopy. Phase purity of the precursors, the calcium sulfate dihydrate and the hydrothermal product formed with different molar ratios, was determined by X-ray diffraction equipment (XRD).

4.5 Synthesis and characterization of Calcium Sulfate Whiskers with different molar ratio of reactants

4.5.1 Synthesis of Calcium Sulfate Whiskers with different molar ratio of reactants

The optimized temperature and mixing ways from the previous experiments were used to produce calcium sulfate dihydrate by mixing 0.5-1.5 $mol.L^{-1}$ Na_2SO_4 to 0.5-2 mol.L^{-1} $CaCl_2$ at temperature of 25 ^{o}C. A series of experiments were performed in which molar ratio of one reactant was kept constant and other was varied to optimized the reactant's ratio. The two solutions were mixed very slowly by keeping the dripping rate of 3mL.min^{-1}. The stirring speed was kept at (100-250rpm). After mixing the raw materials, the suspension was stirred for 1-2 h. The precursors formed were then put into a small stainless steel hydrothermal synthesis autoclave reactor to convert them into calcium sulfate hemihydrate. Hydrothermal reactor having an inner volume of 50ml, heated (3 ^{o}C.min^{-1}) to 130-150 ^{o}C and kept in isothermal conditions for 4.0-6.0 h. After this, the product was cooled down to room temperature naturally, filtered, washed with distilled water and dried at 105 ^{o}C for 2 h in the oven. The resulted product was calcium sulfate whiskers. Figure 4.4 exhibits the steps in synthesis process.

4.5.2 Characterization

Phase purity of the precursors, the calcium sulfate dihydrate and the hydrothermal product formed with different molar ratios, was determined by X-ray diffraction equipment (XRD). The morphology and the particle size of the samples formed with different molar ratios of reactants were examined by scanning electron microscopy (SEM).

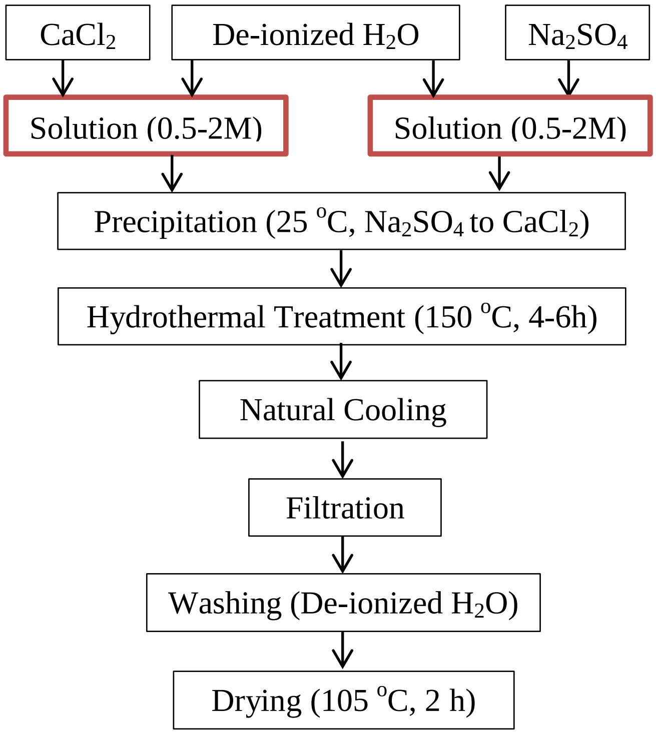

Figure 4.4 Flow chart for the synthesis of CSW with different molar ratio of reactants

4.6 Synthesis and characterization of Calcium Sulfate Whiskers in the presence of additives

4.6.1 Synthesis of Calcium Sulfate Whiskers in the presence of additives

For the production of calcium sulfate dihydrate Na_2SO_4 and $CaCl_2$ having molar ratio 0.5:1 $mol.L^{-1}$ were mixed together and then added 0.2 $mol.L^{-1}$ NaCl and $CaCO_3$ separately into above solution. The stirring speed was kept at (100-250 rpm). After mixing the raw materials and additives, the suspension was stirred for 1-2 h. The precursors formed were then put into stainless steel hydrothermal synthesis autoclave reactor to convert them into calcium sulfate hemihydrate. Hydrothermal reactor was heated (3 $^{o}C.min^{-1}$) to 130-150 ^{o}C and kept in isothermal conditions for 4.0-6.0 h. After this, the product was cooled down to room temperature naturally, filtered, washed with distilled water and dried at 105 ^{o}C for 2 h in the oven. The product formed was calcium sulfate whiskers. Figure 4.5 exhibits major steps of the synthesis process.

4.6.2 Characterization

Phase purity of hydrothermal product formed in the presence of additives was determined by X-ray diffraction equipment (XRD). The morphology and the particle size of the samples formed with different molar ratios of reactants were examined by scanning electron microscopy (SEM).

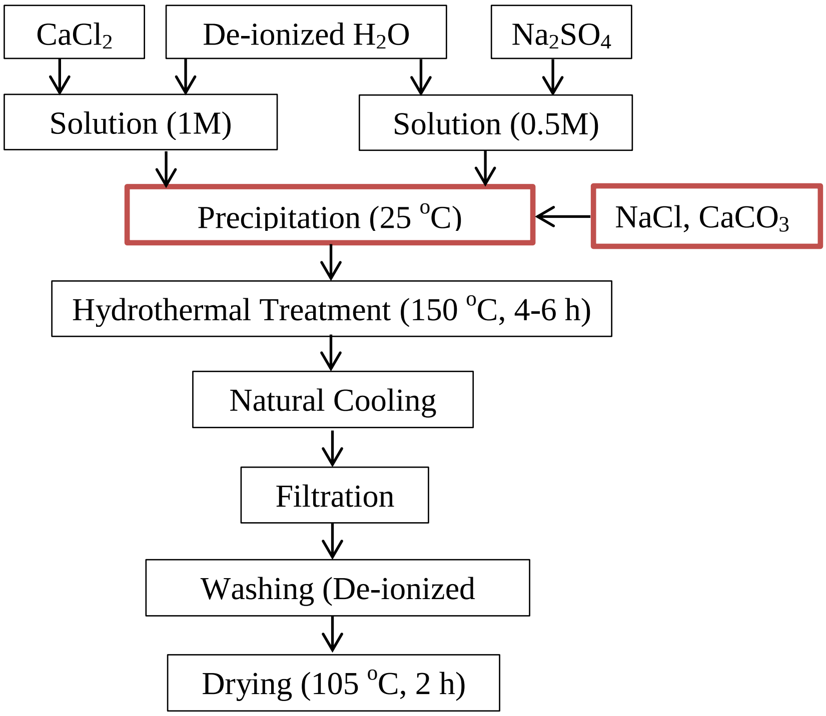

Figure 4.5 Flow chart for the synthesis of CSWs in presence of additives

4.7 Synthesis and characterization of Polycaprolactone- Calcium Sulfate Whiskers (PCL - CSWs) composites

4.7.1 Synthesis of Polycaprolactone- Calcium Sulfate Whiskers composites

Calcium sulfate whiskers prepared in the previous experiments were used for the synthesis of polymer composites. Co-precipitation method was used for the synthesis of polycaprolactone-calcium sulfate whiskers composites. The calcium sulfate whiskers were added to polycaprolactone in different weight percentages i.e. 5%, 10%, 15% and 20 % to study strengthening properties of polycaprolactone-calcium sulfate whiskers composites. A separate experiment was also carried out in which polycaprolactone without CSWs was used for specimen preparation for comparison with the composite. Tetrahydrofuran (THF) was used as a solvent to dissolve the polycaprolactone. The solution formed was stirred for around 2 h. The calcium sulfate whiskers were disseminated separately into appropriate amount of tetrahydrofuran and stirring was done for 2 h. Then polycaprolactone-THF solution and CSWs-THF colloidal solution were mixed together and again stirred for 2 h. Next the blend formed was poured into the ethanol for the co-precipitation of polycaprolactone-calcium sulfate whiskers composites. The composite was separated by filtration and washed with ethanol to remove the tetrahydrofuran from the composite. Then it was dried in vacuum oven at 40 ^{o}C for 10-12 h. The resultant product was PCL-CSWs composite. Figure 4.6 shows the synthesis scheme for PCL-CSWs composite.

4.7.2 Characterization

To examine the tensile and flexural properties of PCL-CSWs composite, universal testing machine (Shimadzu AG-Xplus Shimadzu, Japan) was used. For tensile property test dumb bell shaped specimens of composite were prepared by injection-molding in dies of ASTM D 638 type IV [3, 4]. The tensile tests were performed at ambient temperature and the cross-head speed was kept 2 mm/min. Three test pieces were tested for each composition and the average values were taken as the results. For flexural property test bar-shaped specimens of dimensions 80 mm in length 10 mm in width and 4 mm in thickness was shaped according to the European Standard EN ISO 178 [5]. The cross head speed was set 2 mm/min. Three pieces were tested for each composition and average values were taken as a result. The blank sample i.e.

polycaprolactone without CSWs was also tested for both mechanical property tests. Figure 4.7 shows the specimen for flexural property test.

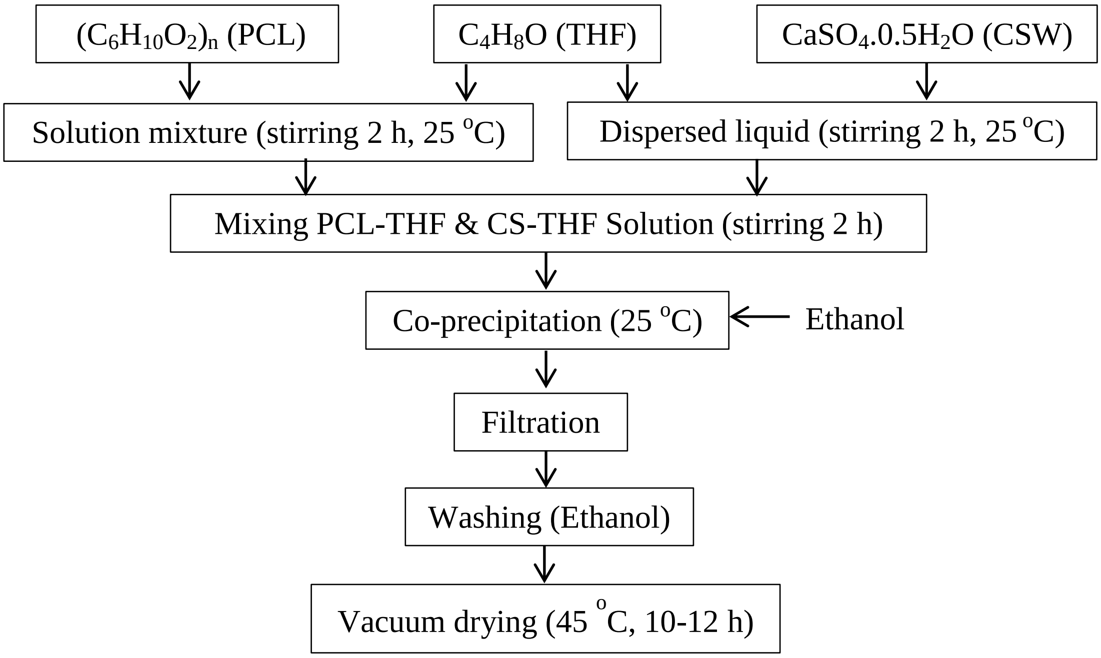

Figure 4.6 Flow chart for the synthesis of CSWs-PCL composite

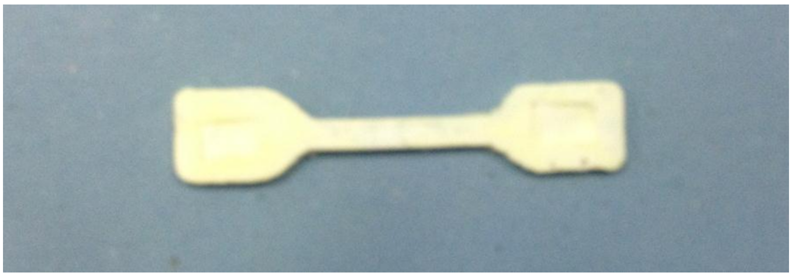

Figure 4.7 Photograph of dumb bell shaped specimen for flexural property test

Summary

For the synthesis of calcium sulfate whiskers, firstly the calcium sulfate dihydrate precursors were prepared by mixing Na_2SO_4 & $CaCl_2$ and then hydrothermal treatment was carried out by hydrothermal synthesis autoclave reactor to convert them into calcium sulfate hemihydrates which are known as calcium sulfate whiskers. Study of process parameters i.e. temperature, molar ratio of reactants and mixing ways of the reactants were carried to optimized the conditions. Initially the reactants were mixed in stoichiometric amounts by adding Na_2SO_4 to $CaCl_2$ and temperature was varied to study its effects. Then temperature and molar ratios of reactants were kept constant and the mixing ways of reactants were studied. Next the optimized temperature and mixing methods were adopted to study the effect of molar ratios of reactants on the morphology and aspect ratio of calcium sulfate whiskers. After optimizing the process parameters, effect of additives i.e. NaCl and $CaCO_3$ were studied on morphology and aspect ratio of CSWs. Afterward the calcium sulfate whiskers-polycaprolactone composites were synthesized by mixing the CSWs and PCL. SEM was used to study the morphology of CSD, CSH and PCL-CSWs composite while phase composition was studied by XRD. The tensile property and flexural tests of the PCL-CSWs composite were carried out by universal testing machine (UTM).

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Chapter 5

Results and Discussion

In this chapter results of the experiments will be discussed for which the details have been given in the chapter 4.

5.1 Characterization of the precursors and hydrothermal product

Figure 5.1 shows XRD pattern of precursors formed at temperature of 25 ^{o}C and the hydrothermal product after hydrothermal treatment. Results reveal that precursors were calcium sulfate dihydrate ($CaSO_4.2H_2O$) by composition while the hydrothermal products were calcium sulfate hemihydrate ($CaSO_4.0.5H_2O$) by composition. All the peaks are exactly matching with cubic structure of the compounds having PDF Card # 33-0311 for precursors, calcium sulfate dihydrate and PDF Card # 45-0848 for hydrothermal product, the calcium sulfate whiskers. There was no indication of any other phase.

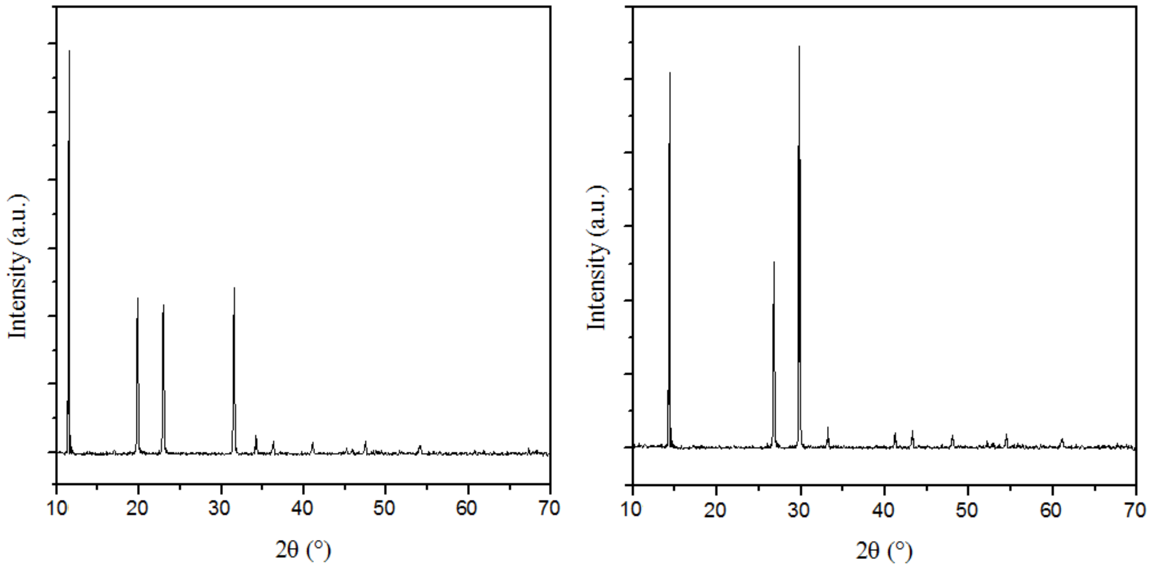

Figure 5.1 XRD pattern of (a) precursors, $CaSO_4.2H_2O$ and (b) hydrothermal product, $CaSO_4.0.5H_2O$

Figure 5.2 exhibits the morphology of the precursors formed at temperature of 25 ^{o}C. Results reveal that precursors consist of irregular structures having length of 5-25 µm and width of 1-7 µm.

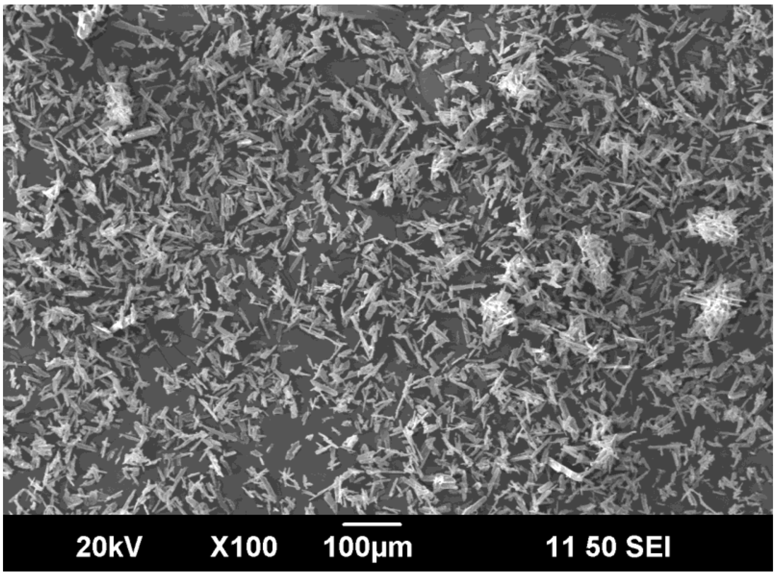

Figure 5.2 SEM Image of Precursors formed at temperature of 25 °C

5.2 Effect of temperature on the synthesis of calcium sulfate whiskers

Figure 5.3 displays the morphology of calcium sulfate whiskers formed at temperature of 25 °C, 55 °C and 85 °C by adding Na_2SO_4 to $CaCl_2$ in stoichiometric ratio for the formation of precursors. The whiskers have high aspect ratio for which the precursors were prepared at 25 °C while the whiskers formed at 55 °C and 85 °C have no uniformity in shape and have low aspect ratio. The increase of temperature leads to increase of precursor's size and hydrothermal product became more non-uniform and thicker as the temperature increased from 25 °C to 85 °C. The whiskers prepared at 25 °C had length of 120-200 μm and diameter of 0.5 - 8 μm. The variation of morphology with the temperature can be explained on the basis of supersaturation at varying temperatures. Supersaturation (S) is defined by the equation 5.1.

$$S = \frac{[Ca_4^{2+}][SO_4^{2-}]}{K_{sp}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 5.1$$

Where

S is the supersaturation

K_{sp} is the equilibrium constant

$[Ca^{2+}]$ and $[SO_4^{2-}]$ are concentration of the soluble Ca^{2+} and SO_4^{2-} respectively.

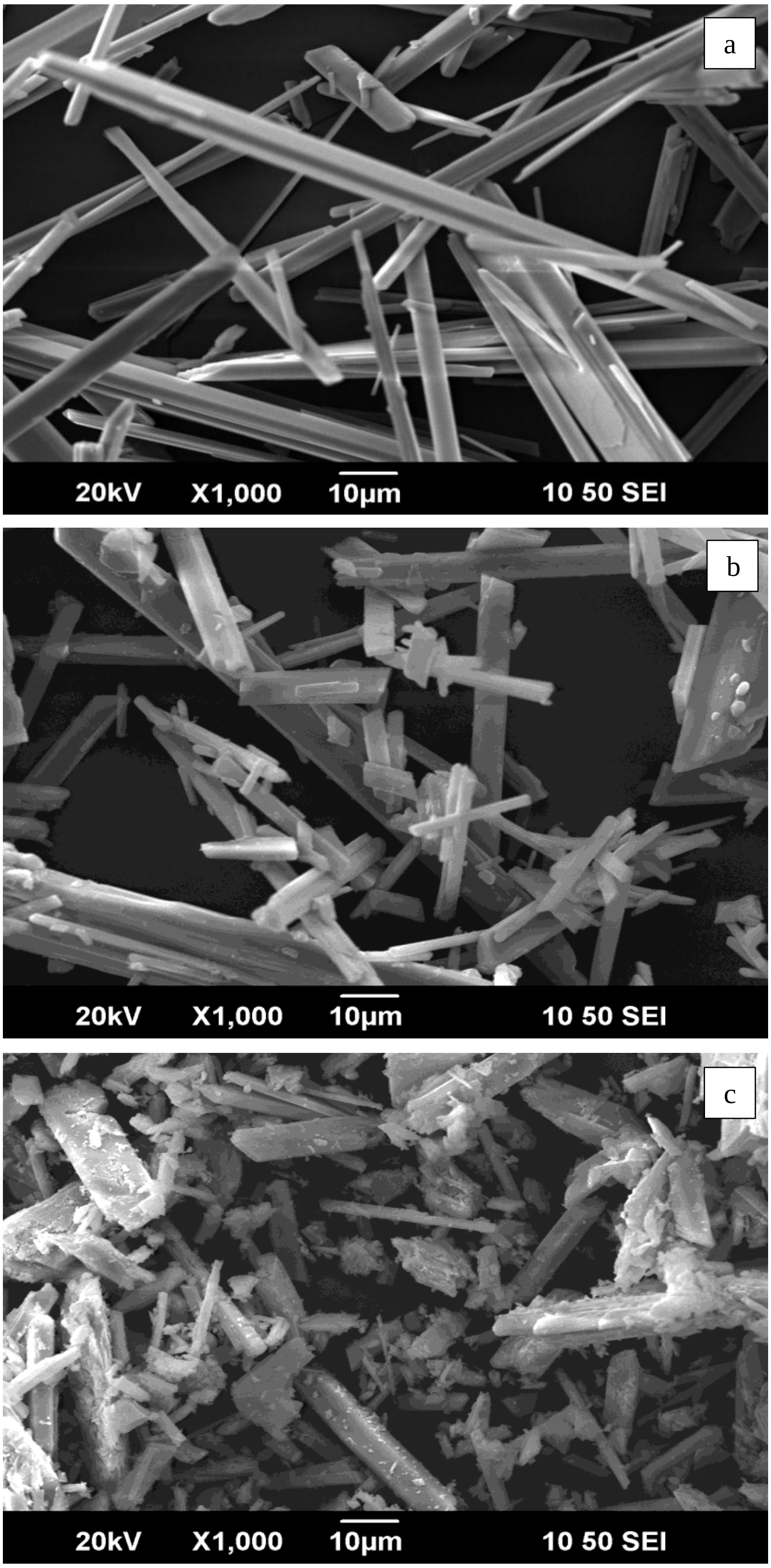

Figure 5.3 SEM Image of CSWs formed at temperature (a) 25 ^{o}C, (b) 55 ^{o}C and (c) 85 ^{o}C

Table 5.1 Effect of temperature on supersaturation of $CaSO_4.2H_2O$

Temperature ^oC	Equilibrium constant (K_{sp})	Supersaturation (S)
25	3.10×10^{-5}	201.5
55	2.35×10^{-5}	270.4
85	1.42×10^{-5}	441.6

Table 5.1 provides relationship among temperature (T), supersaturation (S) and equilibrium constant (K_{sp}). It is examined from the data that by increasing the temperature, the K_{sp} value of $CaSO_4.2H_2O$ decreased. Hence, the supersaturation at low temperature is small as compared to high temperature. Super-saturation is associated with growth rate of the crystals as stated in crystallinity theory. The more supersaturation, greater the growth rate of the crystals. Formation of $CaSO_4.2H_2O$ precursors is linked directly with the growth rate of the crystals. Low temperature favored the small growth rate so the precursors with smaller size were formed and resultant hydrothermal product with uniform shape was formed. So the temperature of 25 ^oC is more suitable as compared to 55 ^oC and 85 ^oC for the formation of precursors with smaller size and the corresponding hydrothermal product, the calcium sulfate whiskers with uniform shape and high aspect ratio.

5.3 Effect of mixing methods of the reactants

Figure 5.4 exhibits the effects of mixing methods of the reactants on the morphology and aspect ratio of calcium sulfate whiskers. The reactants were reacted in stoichiometric ratio and at temperature of 25 ^oC.

The mixing ways of reactants has a direct effect on the size of precursors and the morphology of the hydrothermal product formed. By adding the Na_2SO_4 to $CaCl_2$ the precursors with small size were formed and the resultant hydrothermal product with large aspect ratio was formed while addition of $CaCl_2$ to Na_2SO_4 favored the precursors with larger size and subsequent hydrothermal products with relatively small aspect ratio and unequal shape were formed.

In Figure 5.5 the supersaturation and K_{sp} is plotted against time which shows that the values of supersaturation are greater than K_{sp} which promoted the crystal growth. It is also shown that values for line ‘a’ are larger than that of line ‘b’, so supersaturation for the line ‘a’ is greater than line ‘b’ and the precursors size is also bigger for line ‘a’ as compared to line ‘b’. So supersaturation has a direct effect on the particle size of the precursors. For the formation of calcium sulfate whiskers with high aspect ratio, adding Na_2SO_4 to $CaCl_2$ is more favorable way as compared to $CaCl_2$ to Na_2SO_4 to mix the reactants.

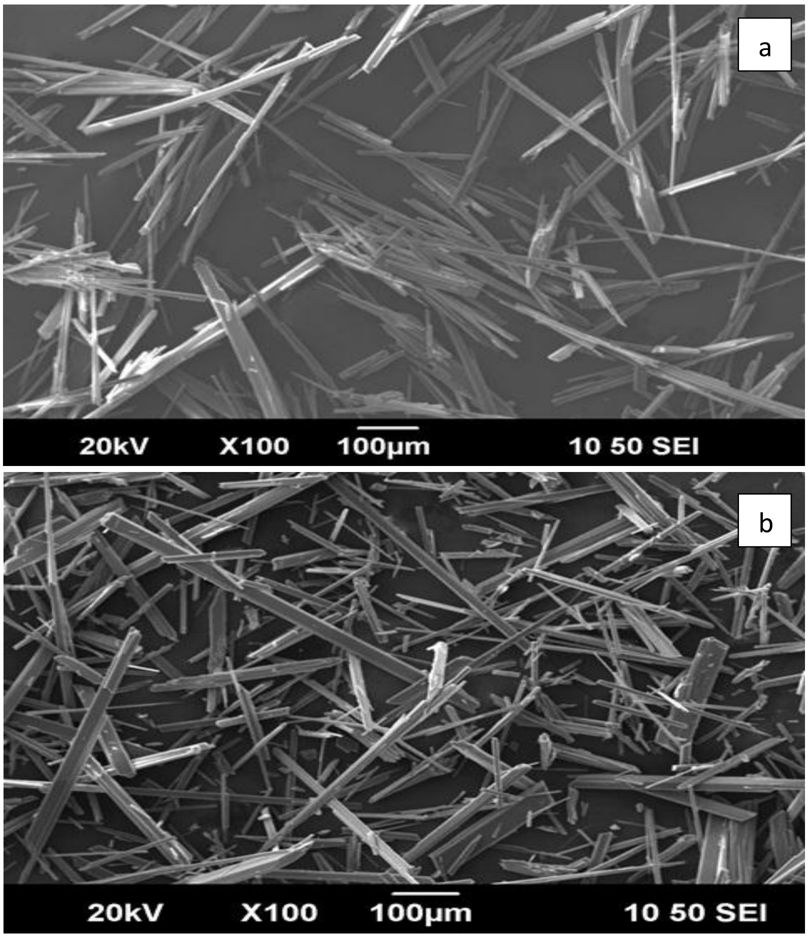

Figure 5.4 SEM Image of CSWs by mixing (a) Na_2SO_4 to $CaCl_2$ (b) $CaCl_2$ to Na_2SO_4

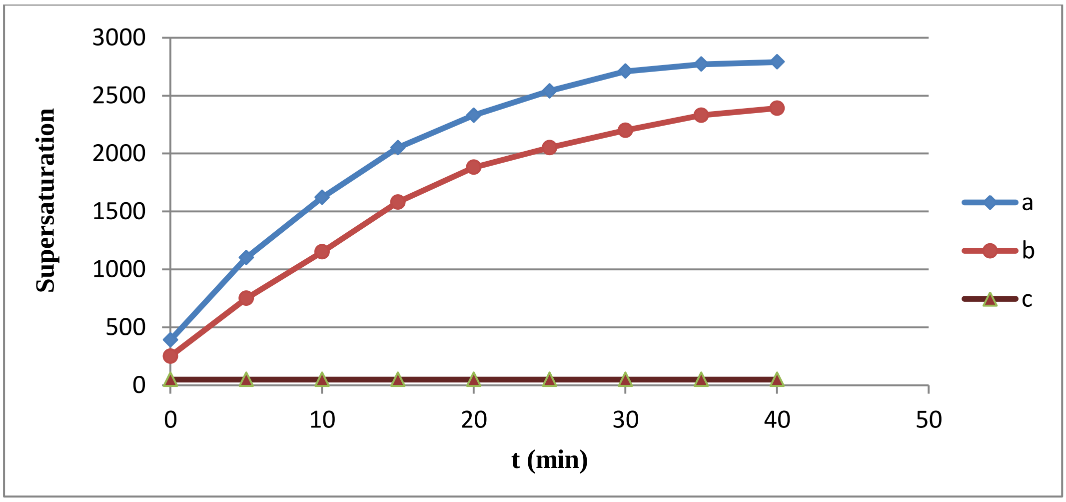

Figure 5.5 Effect of mixing methods of reactants on the supersaturation (a) $CaCl_2$ to Na_2SO_4 (b) Na_2SO_4 to $CaCl_2$, (c) K_{sp} of calcium sulfate dihydrate

5.4 Effect of molar ratio of reactants

To study the effects of molar ratio, the reactants were mixed by adding Na_2SO_4 to $CaCl_2$ at temperature of 25 ^oC, conditions that were optimized in previous experiments. The effect of variation of molar ratio on the morphology of calcium sulfate whiskers can be explained on the basis of supersaturation. Figure 5.6 exhibits the curves for supersaturation verses time for different molar ratios of reactants. Figure 5.7 shows the effects of molar ratio of the reactants on the morphology and aspect ratio of calcium sulfate whiskers. The supersaturation was highest for molar ratio 1:0.5 and lowest for molar ratio 0.5:1 in case of Na_2SO_4 to $CaCl_2$. According to the von Weimarn's theory of relative supersaturation, the relative supersaturation is inversely proportional while the degree of supersaturation is directly proportional to the particle size of precipitates. Relative supersaturation (RSS) is defined by the equation 5.2.

$$RSS = \frac{A - B}{B} \quad \text{...5.2}$$

Where A is actual concentration of solute when precipitation starts, B is the equilibrium concentration of solute in the saturated solution and A-B is degree of supersaturation. So the ratio A-B/B is the von Weimarn's ratio. As the degree of supersaturation is directly proportional to particle size so in order to make the precipitates with small size the conditions are to be adjusted to make the supersaturation ratio small to get precipitates with small size.

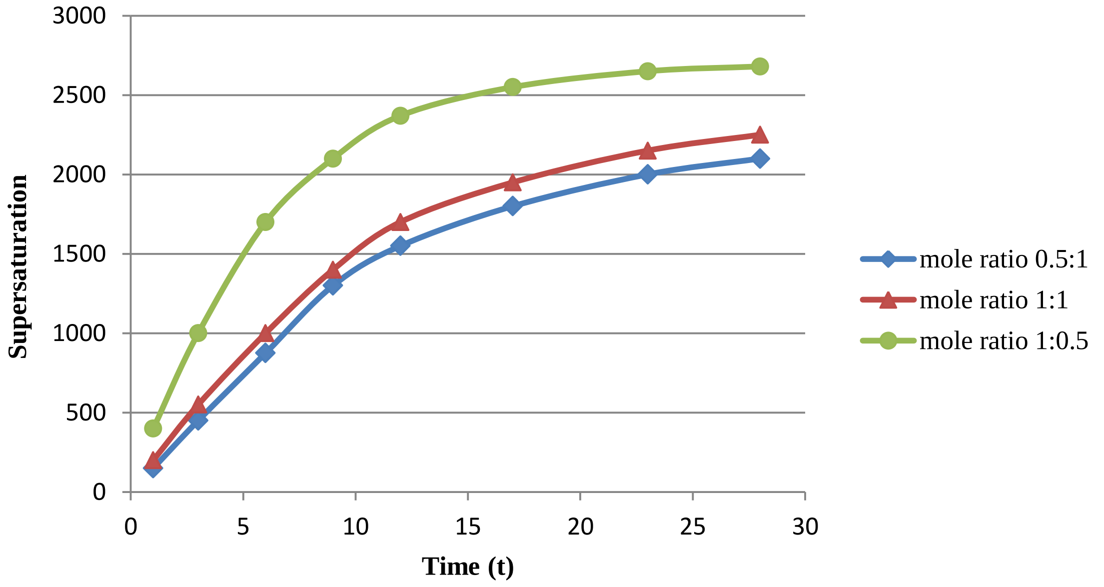

Figure 5.6 Effect of moral ratios of reactants on supersaturation

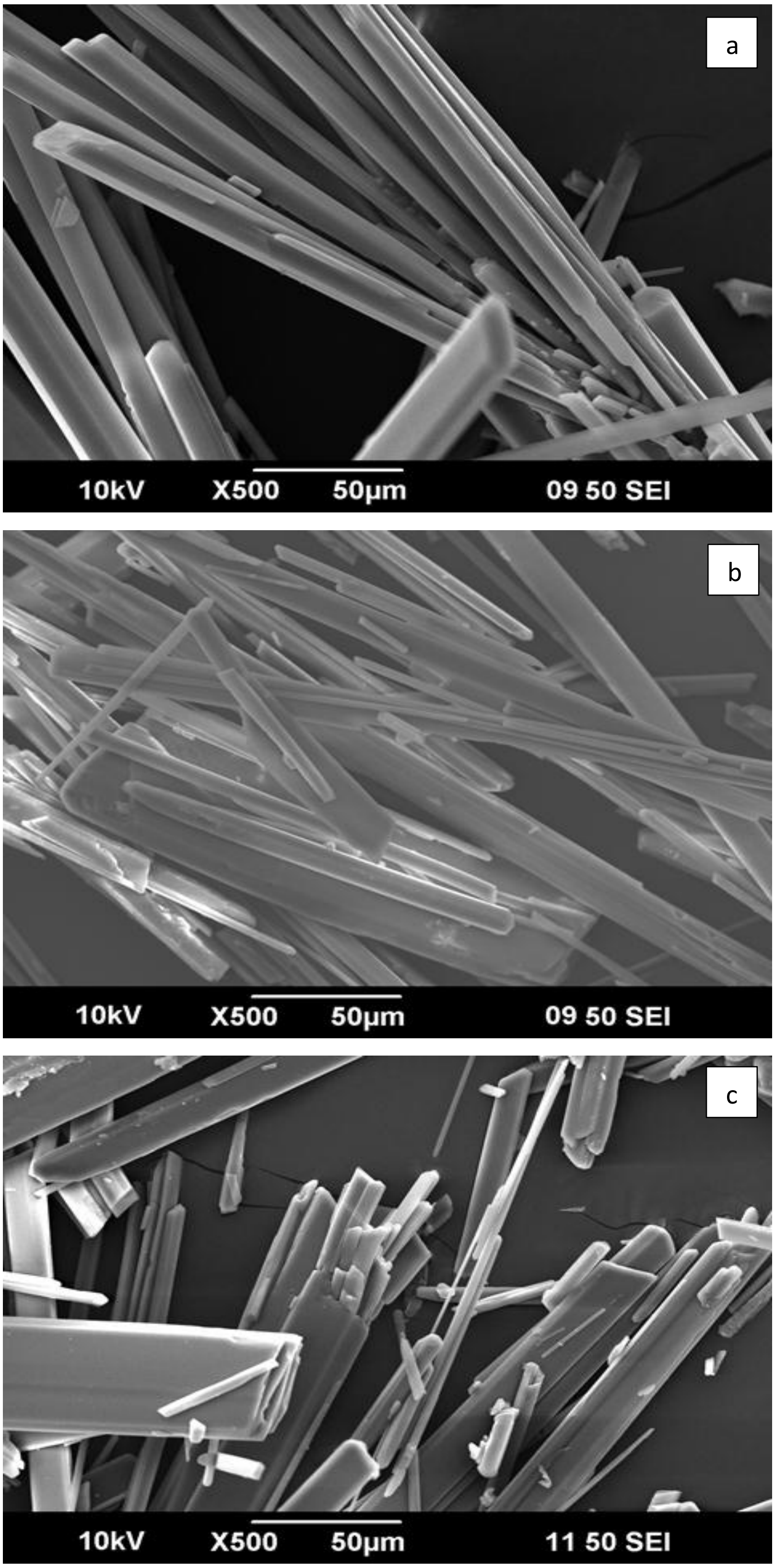

Figure 5.7 SEM Images of CSWs formed with molar ratios (a) 0.5:1 (b) 1:1 (c) 1:0.5

Hence Na_2SO_4 to $CaCl_2$ that were mixed in molar ratio 0.5:1 favored the precursors with small crystal size and corresponding hydrothermal product with large aspect ratio.

5.5 Effect of additives on morphology and aspect ratio of CSWs

Figure 5.8 shows the effect of sodium chloride (NaCl) and Figure 5.9 shows the effects of calcium carbonate ($CaCO_3$) on the morphology and aspect ratio of CSWs. In the presence of NaCl, the shape deformed to irregular and the length to diameter (L/D) ratio of whiskers decreased and as the concentration of the NaCl increased from 0.2-0.5 mol L^{-1} the aspect ratio decreased further. The effect of $CaCO_3$ was found more prominent on the morphology of the whiskers. The whiskers became thicker and their L/D ratio decreased. By the addition of NaCl the spectator's ions increased which hindered the effective collusions of reactants to make the precursors and hydrothermal product. This effect is also related with supersaturation. In the presence of additives the supersaturation increased which led to the formation of precursors with larger size and corresponding hydrothermal product with non-uniform shape and small aspect ratio.

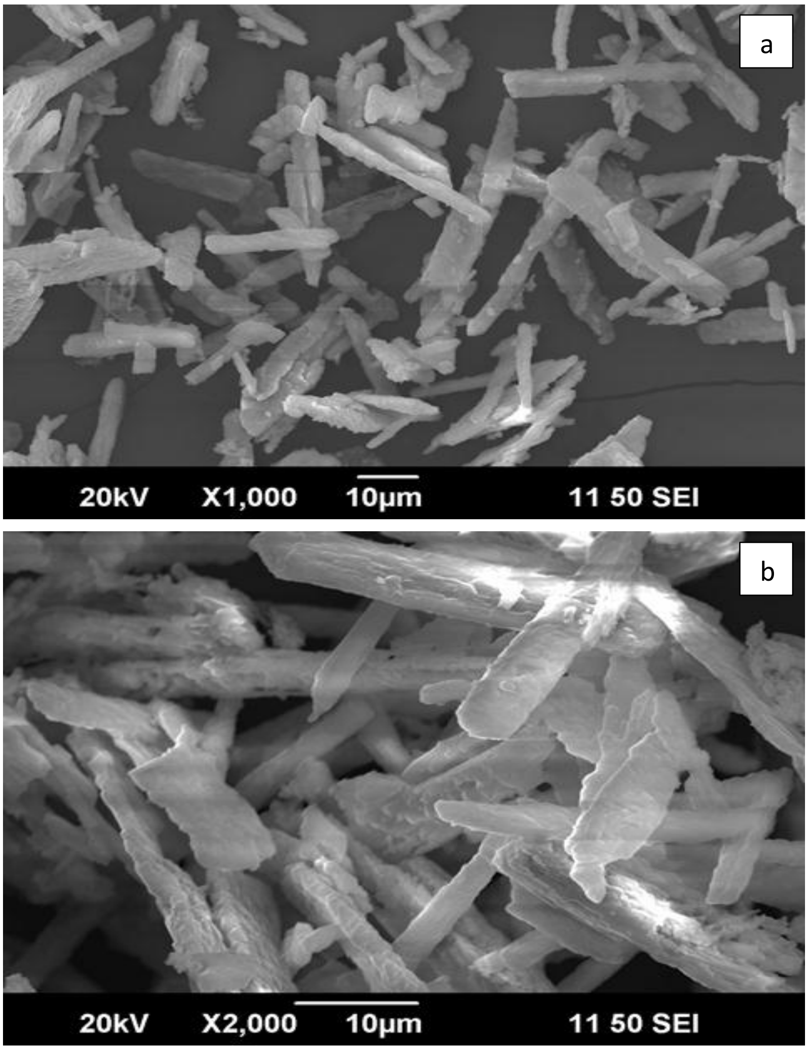

Figure 5.8 Effect of NaCl on CSWs: a- 0.2 (mol L^{-1}), b- 0.5 (mol L^{-1})

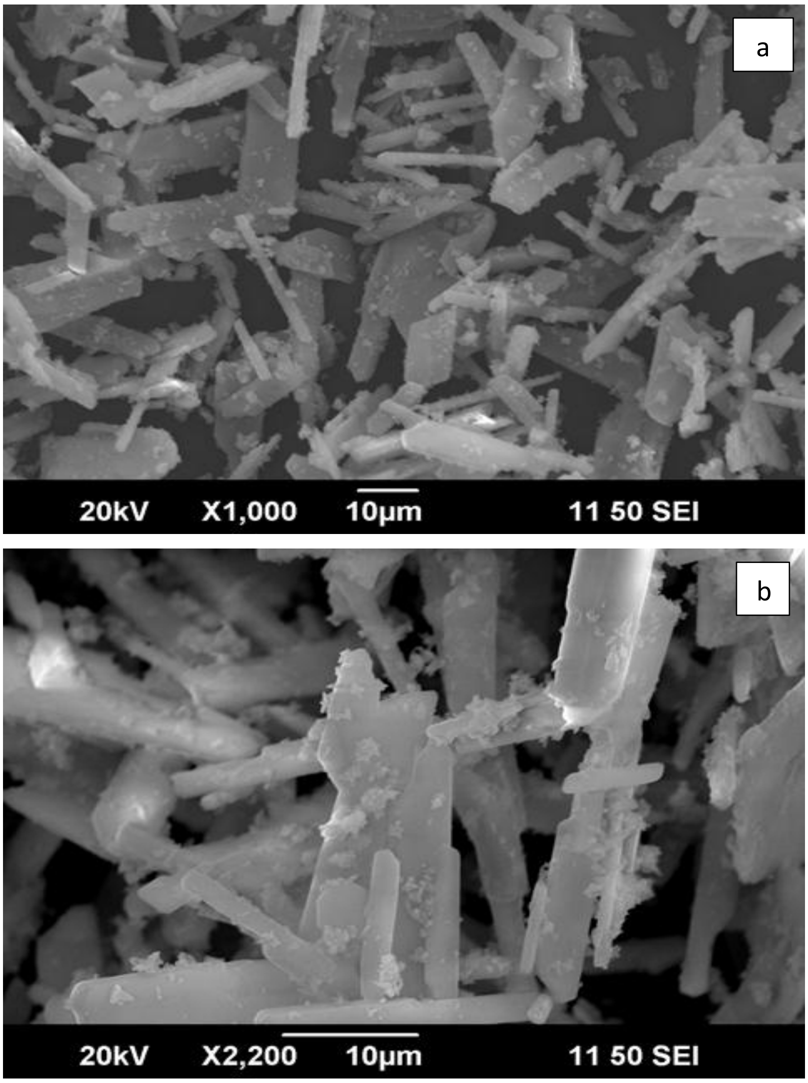

Figure 5.9 Effect of $CaCO_3$ on CSWs a-0.2 (mol L^{-1}), b-0.5 (mol L^{-1})

5.6 Mechanical properties of PCL-CSWs composites

- **Tensile strength**

Tensile strength is defined as the maximum stress the material can withstands before failing or breaking. This is also called ultimate tensile strength (UTS).

- **Flexural strength**

Flexural strength is also known as bending strength and is defined as ability of material to resist the deformation under load.

Figure 5.10 shows stress strain curve for pure PCL and PCL-CSWs composite with 5 wt. % and 10 wt. % respectively. From the figure it can be seen that curve for the pure PCL has less slope as compared to other two curves in which calcium sulfate whiskers are added in 5 wt. % and 10 wt. % in PCL. The slope of both composites is same with in the elastic region of stress strain curve but in the plastic region, the slope is higher for PCL-CSWs composite with 10 wt. % as compared to 5 wt. % which reveals that whiskers with greater quantity can increase strength of the composite more. Table 5.2 displays the data taken from stress strain curves. So the tensile strength increases with the addition of 5 wt. % of CSWs and further increases with 10 wt. %.

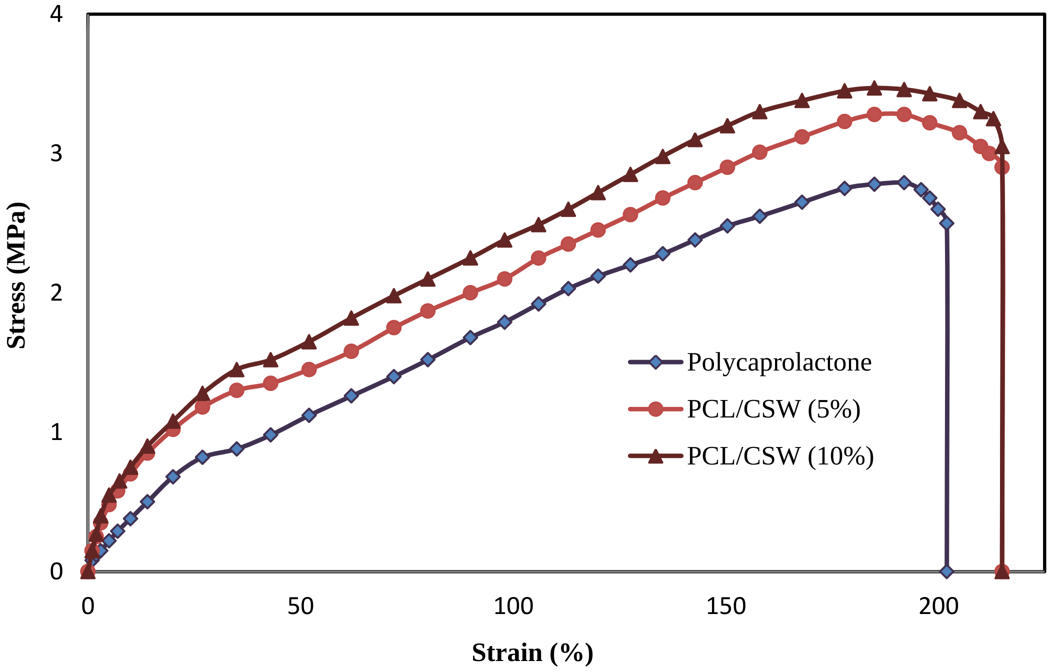

Figure 5.10 Representative curves for tensile test of PCL-CSWs composite

Table 5.2 Results of tensile property test

Composition	Tensile Strength (MPa)	Strain at Break (%)
PCL	2.9	202
PCL-CSWs 5%	3.3	215
PCL-CSWs 10%	3.5	218

Figure 5.11 and Figure 5.12 exhibit the results of flexural property test for the pure PCL and PCL-CSWs composites. Flexural strength is calculated by the equation 5.3

$$\sigma_f = \frac{3FL}{2bh^2} \qquad \text{.....................} 5.3$$

Where

F is the applied force, (N)

L is the span, (mm)

b is the width of specimen, (mm)

h is the thickness of specimen, (mm)

Flexural modulus is calculated by equation 5.4

$$E_f = \frac{L^3 m}{4bd^3} \quad \text{..} 5.4$$

Where

E_f is the flexural modulus, (MPa)

L is sport span, (mm)

m is gradient (slope) of initial straight-line portion of load deflection curve, (N/mm)

b is the width of specimen, (mm)

d is the depth of specimen, (mm)

Results revealed that flexural strength and flexural modulus is low for the pure PCL while it is higher for PCL-CSWs composite. The flexural strength and flexural modulus increases with the addition of CSWs from 5 wt. % to 15 wt. % and then decreases as the CSWs are added in 20 wt. %. The values of flexural strength and flexural modulus at 15 wt. % are 17 MPa and 720 MPa respectively. These results can be explained on basis of load transfer theory, according to which the stress is shifted from the polymer matrix to the whiskers through interfacial layer [1, 2]. As the modulus of the whiskers is higher than that of polymer matrix so they can tolerate part of stress by disbanding load in matrix. Hence the strength of the PCL-composite is increased by the addition of whiskers. This theory also proposes that whiskers with high aspect ratio increase the strength of composite more than whiskers with small aspect ratio.

The dispersion of whiskers in polymer matrix is key element affecting the strength of PCL-whiskers composite. The mechanical properties of the composite depreciate when the agglomeration of the whiskers occur in the matrix [3]. In flexural property test, the flexural strength and flexural modulus decreased by the addition of 20 wt. % mainly due to the agglomeration of whiskers in the polymer matrix, moreover the maximum spaces were occupied in the matrix and no additional load can be sheared. So the dispersion of whiskers is the leading factor affecting the strength of PCL-whiskers composites.

Results of flexural property test reveal that change trend for flexural modulus is similar to the change trend of flexural strength for the composites. It directs that although CSWs belong to rigid filler which can improve the rigidity of materials[4], but rigidity cannot be improved infinitely with addition of whiskers.

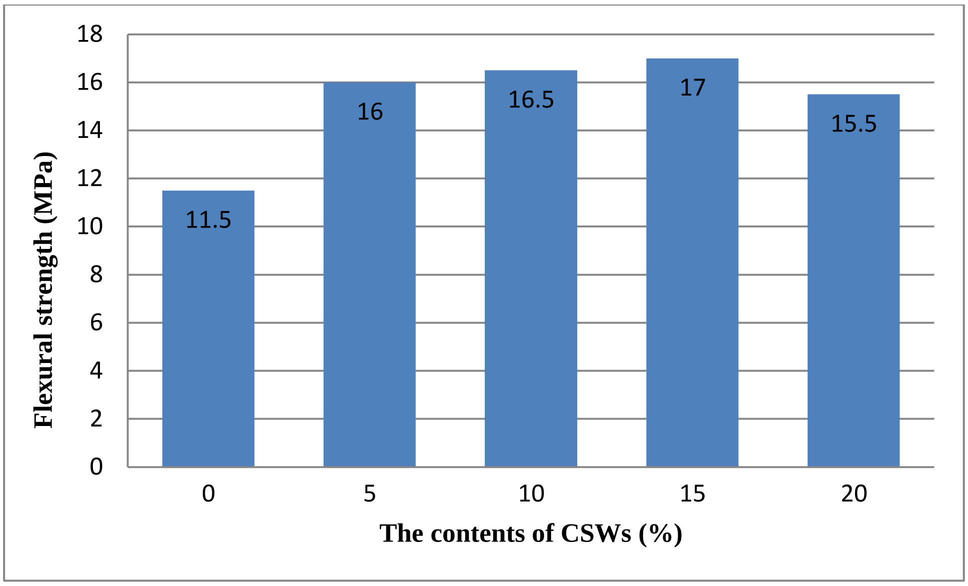

Figure 5.11 Effect of wt. % age CSWs on the flexural strength of PCL-CSWs composites

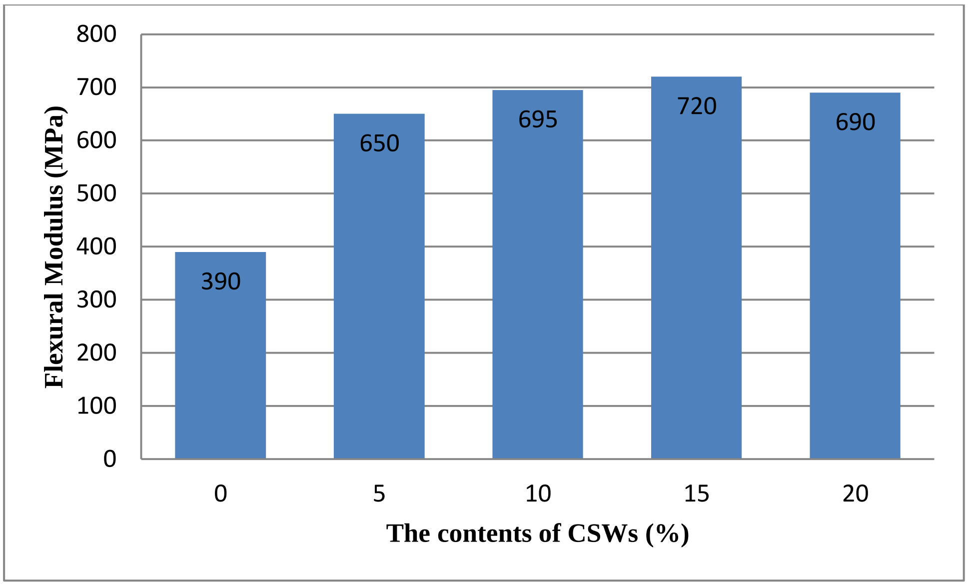

Figure 5.12 Effect of wt. % age of CSWs on the flexural modulus of PCL-CSWs composites

Summary

For the characterization of precursors and hydrothermal product X-ray diffraction (XRD) and scanning electron microscope (SEM) was used. The phase purity of precursors ($CaSO_4.2H_2O$) and hydrothermal product ($CaSO_4.0.5H_2O$) was determined by XRD and morphology was observed by SEM. The effects of process parameters i.e. temperature, molar ratio of reactants and mixing ways of the reactants on the morphology and aspect ratio were studied. The optimum conditions found were temperature 25 ^oC, molar ratio of Na_2SO_4 to $CaCl_2$ 0.5:1 and by adding Na_2SO_4 to $CaCl_2$ for the synthesis of calcium sulfate whiskers with high aspect ratio. For enhancement of mechanical strength of polycaprolactone, calcium sulfate whiskers with different percentage were added. Results revealed the optimum percentage of CSWs to be 15% after which the strength of composite began to decrease.

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Conclusions

In this work, calcium sulfate whiskers were successfully synthesized from the calcium chloride discharged from the Solvay process by hydrothermal method and then these whiskers were used as reinforcing material in polycaprolactone to form polycaprolactone-calcium sulfate whiskers (PCL-CSWs) composites.

The optimum process parameters for the synthesis of calcium sulfate whiskers came to be; temperature of 25 ^{o}C, molar ratio of sodium sulfate to calcium chloride 0.5:1 and by adding sodium sulfate to calcium chloride as a way of mixing the reactants. The morphology and aspect ratio of the whiskers was strictly associated with temperature and reactant's molar ratio. Moreover slow mixing of reactants made the precipitates with small sizes which favored the corresponding hydrothermal product with uniform structure and large aspect ratio. The whiskers formed in this way had length of 150 - 200 µm, width of 0.5 - 8 µm and aspect ratio of 25 - 120. The pH of the medium was almost in neutral range and it had no effect on the morphology and aspect ratio of whiskers. The additives i.e. sodium chloride (NaCl) and calcium carbonate ($CaCO_3$) altered the morphology of calcium sulfate whiskers and reduced the aspect ratio so these additives can't be added calcium sulfate whiskers during their synthesis.

For the synthesis of polycaprolactone-calcium sulfate whiskers (PCL-CSWs) composite, co-precipitation method was used. The concentration and mixing of calcium sulfate whiskers in the polycaprolactone are the main factors affecting the mechanical properties of the composite formed. Whiskers with high aspect ratio increase the mechanical properties of composite more than whiskers with small aspect ratio. The flexural strength was highest with 15 wt. % addition of calcium sulfate whiskers, after this agglomeration of whiskers occurred in the polymer matrix which reduced the mechanical strength. Hence calcium sulfate whiskers are suitable for the reinforcement of polymer composite.

From the process study it can also be concluded that synthesis of calcium sulfate whiskers are feasible from calcium chloride discharged from the Solvay process and these whiskers can be used as reinforcing material in rubber, plastic and polymer composites.

Calcium Sulfate Whiskers: A review on preparation methodologies

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Abstract

Environment friendly, cost effective, non-toxic and thermally stable calcium sulfate whiskers (CSWs) are widely used as reinforcing material in paper making, rubber, polymer composite and plastic. Due to wide range of applications of CSWs much consideration has been given to their preparation in cost effective ways. The size and shape of the CSWs play a vital role in their applications. The interest has been growing in developing the calcium sulfate whiskers with controlled morphology and high aspect ratio. This review focus on the different methodologies for the preparation of CSWs that include (a) hydrothermal method, (b) salt solution method, (c) organic-water system, (d) microwave assisted route, (e) ultrasound-assisted method and (f) reverse microemmulsion method. This review summarizes the effects of process parameters i.e. temperature, molar ratio of the reactants, pH & pressure, and additives (inorganic and organic) on the growth and morphology of CSWs. This review also covers the modifications made in the exiting processes to control the morphology of CSWs. Moreover the hydrothermal method produces CSWs with controlled morphology and high aspect ratio. For the commercial production of CSWs a cheap source of raw material is proposed.

Keywords: Calcium sulfates, whiskers, preparation methods, micro/ nano structures

1. Introduction

Calcium sulfates (CS) are important family of minerals that are widely used as filler material in paper making, plastic, rubber, pigments and polymer composite [1, 2]. Total of six forms of CS are known of which three forms occur during the environmental and industrial precipitation process which comprise calcium sulfate dihydrate CSD ($CaSO_4.2H_2O$), calcium sulfate hemihydrate CSH ($CaSO_4.0.5H_2O$) and anhydrite CSA ($CaSO_4$) [3, 4]. Calcium sulfate in hemihydrate (HH) form are known as calcium sulfate whiskers. Calcium sulfate HH is most commonly used ones in ample types of calcium sulfates. The performance of calcium sulfate HH is strictly connected with the crystal size and morphology. Therefore, the morphological control of HH is a precondition to acquire the proper performance to meet the desired applications [5-8]. Thus hemihydrate whiskers, nano rods, nano sheets, wires and long columns are produced by (a) hydrothermal method, (b) the salt solution method, (c) organic-water system, (d) microwave assisted route, (e) ultrasound-assisted method and (f) w/o microemmulsion or reverse microemmulsion method.

A lot of strategies have been applied to control the HH morphology and aspect ratio in above mentioned methods that include manipulation of pH, the electrolyte concentration and use of crystal growth modifiers. Some researchers studied the effect of organic surfactants for instance cetyltrimethyl ammonium bromide (CTAB), sodium dodecyl sulfate and citric acid on the formation of calcium sulfates while other used solutions of inorganic salts such as NaCl, $CaCl_2$, $MgCl_2$, and KCl as a dehydration media or additives to transform the DH into HH by salt solution and hydrothermal method.

Some investigators used raw materials from different sources for the preparation of hemihydrates. For instance Kangbi Luo et al. used sodium sulfate and calcium chloride for calcium sulfate preparation, Zongyou Pan et al. used $Ca(OH)_2$ and H_2SO_4 for precipitation of calcium sulfate, Hua He et al. prepared the phosphogypsum (PG) based $CaSO_4.0.5H_2O$ whiskers, Xingfu Song et al. used waste $CaCl_2$ and H_2SO_4 for preparation of calcium sulfates by reactive crystallization.

This review discourses the methods used for the production of calcium sulfate HH by using different raw material and from different sources. Effects of different process parameters and additives on the morphology and size of calcium sulfates whiskers formed are considered. This review summarizes the modifications made in the exiting processes to control the morphology of CSWs. Moreover the hydrothermal method produces CSWs with controlled morphology and high aspect ratio. For the commercial production of CSWs a cheap source of raw material is proposed.

2 Preparation methods for calcium sulfate hemihydrate (CS-HH)

Various methods for preparation of calcium sulfates are reported in the literature including (a) the salt solution method, (b) organic-water system, (c) microwave assisted route, (d) w/o microemmulsion or reverse microemmulsion method, (e) ultrasound-assisted method and (f) hydrothermal method

2.1.1 Salt Solution Method

The general procedure of the method is; a glass reactor is used that is equipped with reflux condenser for vapor reflux and a Teflon stirrer for obtaining homogenous suspension. The temperature of the reactor is monitored by thermometer. Temperature has typically range of 110 to 120 ^{o}C. In a typical synthesis 30 wt. % calcium chloride solutions with various reactions medium are used for the preparation of calcium sulfate hemihydrate. The solution is constantly stirred for half an hour to obtain uniform suspension. Then the solution is transferred to three neck flask that is preheated to certain temperature with stirring. In flask calcium sulfate dihydrate powder is added and reacted for about 48 hours. After that the slurry is filtered and dried at 110 ^{o}C for 30 minutes in an oven [9-11].

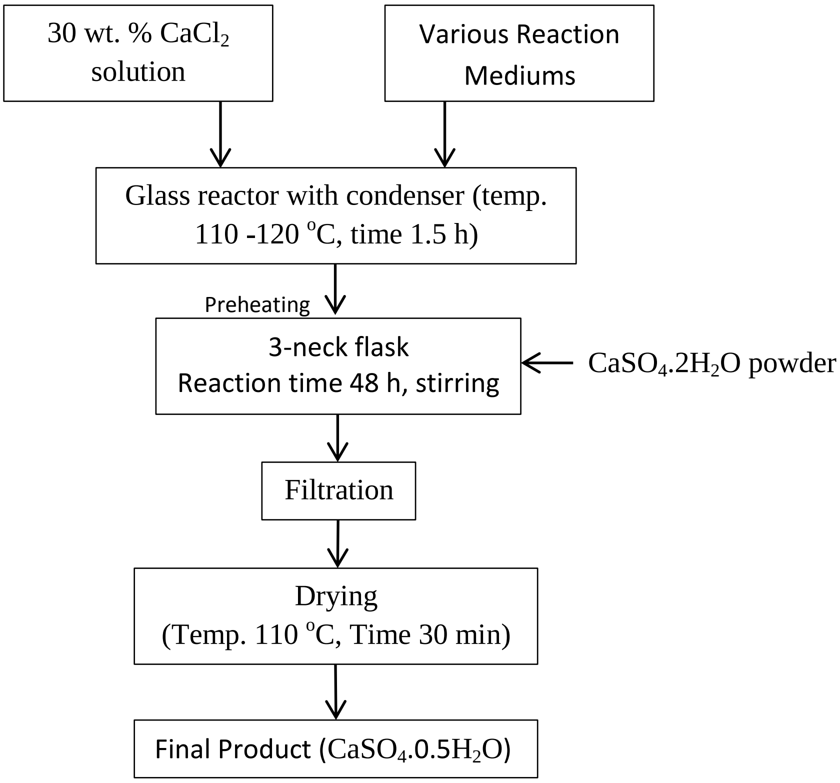

Figure 1 Schematic diagram for synthesis of calcium sulfate HH by salt solution method

Many investigators have reported the salt solution method for the formation of calcium sulfate whiskers over the last ten years which mainly focus on solution composition.

Liuchun Yang et al. studied the growth of calcium sulfate hemihydrate in K-Ca-Mg-Cl-H_2O system at elevated temperature and investigated the effect of Mg^+ and K ions on the growth. They find out optimum composition of solution for the growth of calcium sulfate HH. Research results revealed that HH crystals in concentrated $CaCl_2$ solution remain as a metastable phase for several hours and $CaCl_2$ solutions supersaturated with calcium sulfate is suitable for HH preparation. Crystal growth rate is affected by presence of impurities in several ways. Impurities not only affect the equilibrium concentration and super saturation but also modify the surface charge of crystals [12]. Mg^+ and K^+ ions enhance the growth mechanism of HH which is due to increased initial super saturation initiated by solubility decreasing effects [13]. K^+ ions reveal more accelerating effect on growth than Mg^+ with highest growth rate being at 0.01 M K^+ ions. Higher temperature favors the growth of HH. [14, 15].

Jen-Chang Yang et al. developed a one pot salt solution method for the direct preparation of calcium sulfate hemihydrates in $CaCl_2$ solution and studied the effect of reaction time, reaction temperature and concentration of $CaCl_2$ on the synthesis of calcium sulfate hemihydrate. Calcium sulfate was prepared by mixing the K_2SO_4 and $Ca(NO_3)_2.4H_2O$ under various concentration of $CaCl_2$ and reaction temperature. Results indicated that calcium sulfate dihydrate was found to be an intermediate compound that converts to calcium sulfate hemihydrate during the synthesis process. Increasing the $CaCl_2$ concentration enhanced the conversion of calcium sulfate dihydrate to calcium sulfate hemihydrate. The phases of calcium sulfate hydrates could be controlled by changing the reaction temperature and $CaCl_2$ concentration [16].

Thomas Feldmann et al. carried out process study on the crystal growth kinetics of calcium sulfate HH in nearly constant supersaturated HCl-$CaCl_2$ solutions by taking on semi batch procedure as means of maintaining principally constant super saturation. Process study discovered the influence of following parameters on the crystal growth: temperature (70-90 ^oC), specific power input of stirring (0.02-1.29 w/kg) and equimolar inflow rate of Na_2SO_4 and $CaCl_2$ (0-0.6 mol/h) [17]. Results revealed that crystal growth rate is directly related to reagents inflow rate with optimal value obtained at 0.3 mol h^{-1}. At this rate the yield obtained was 150% of initial mass of seed crystals. The crystal growth process followed the von Weimarn law of crystallization, which relates the particle size with super saturation. As the crystal growth rate increases the width of particle size distribution decreases, a behavior ascribed to a size dependent growth process. The quality of HH crystals was improved not only in terms of crystal size but also in its aspect [18].

Jingwei Mao et al. studied the effects of citric acid on metastability of calcium sulfate hemihydrate in $CaCl_2$ solution. The HH was chosen to show the metastable lifetime (MLT) dependence on the temperature of 25-95 ^oC and citric acid concentrations of 0.1-1mM in salt solution. Results indicate that calcium sulfate HH is metastable form of calcium sulfate phases. Although it is initially precipitated from the solution, it tends to hydrate to dihydrate (DH) or dehydrate to anhydrite (AH) [19]. Its MLT exhibited a short period when converted dihydrate (DH), while a large span was expected when transformed to anhydrite (AH) in concentrated $CaCl_2$ solution [20]. Citric acid prompted the expansion of MLT, particularly in the temperature range of 45-75 ^oC. The expansion of MLT will help for HH purity control by hindering the hydration to DH and dehydration to AH during its preparation. It provided efficient method to adjust the MLT of metastable crystal to control the transformation [21].

Baohong Guan et al. developed a method for preparation of calcium sulfate α-hemihydrate on pilot scale from flue gas desulfurization (FGD) gypsum in mixed salt solution under atmospheric pressure. The impact of salt solution recycling on the conversion of HH from FGD gypsum were examined and compared with that of laboratory scale by concentrating on dehydration rate of FGD gypsum, the crystal morphology and chemical composition. For comparison the recycled salt solution is used as crystallization medium without addition of any salt in the laboratory scale while in pilot scale experiment the concentration of Ca^{2+}, Mg^{2+} and K^+ ions can be kept in certain range through recycling salt solution and by the addition of salts. Process study revealed that experimentation carried out in the laboratory, the salt solution is available to convert the FGD gypsum into HH after recycling seven times without addition of salts. In the pilot experiments, after eight times recycling and by the addition of 20-30% salts, can be employed for the preparation of HH from FGD gypsum.

The residence time for in the laboratory is 5.0-6.0 h while it is 3.5-6.0 h for pilot scale. The HH with prismatic morphology and high strength can be prepared in recycling salt solutions. The recycling salt solution can decrease the consumption of crystallization medium, consequently decreasing the production cost [22].

Fan Li et al. synthesized the calcium sulfate hemihydrate (CSH) powders by salt solution method. The morphologies were modified by altering the pH of reaction solutions and or by adding the succinic acid. Study investigated that the optimum conditions for the conversion of calcium sulfate dihydrate to α-calcium sulfate hemihydrate had a pH of less than 10 without the addition of succinic acid or pH in range 1.5-3.0 with addition of succinic acid. The dissolution of CSD is determined by the acidity of solution. The carboxyl group is provided by the ionized succinic acid in the solution which can chemically absorb on the surface of crystal surface and thus can modify the crystal growth habit. On the other hand, at high pH above 3.0, carboxyl group in the succinic acid strongly interacted with CSD crystals during the dissolution stage, which suppressed the nucleation of CSH crystals [11].

2.1.2 Organic-water system

The overall procedure is as follows: extractant N1923 was used as primary ammine. The SO_4^{2-} ions were extracted from the primary amine in organic phase while Ca^{2+} were extracted into organic solvent by another ammine, bis(ethylhexyl) hydrogen phosphate (HDEHP). $Ca(DEHP)_2$ was prepared by mixing $Ca(NO_3)_2$ aqueous solution with HDEHP heptane in a suitable quantity. The pH of aqueous phase was adjusted to 6.0 by ammonia solution. After reaching at equilibrium stage the organic phase was separated and used in the experiments.

For preparation of primary ammine sulfate, the extractant (primary amine) was dissolved in sulfuric acid solution so that it converts to primary amine sulfate. After the equilibrium was developed between organic phase and aqueous phase, the organic phase was separated for use in the following experiments.$CaSO_4$ crystals were formed by mixing equal volumes of primary amine sulfate in n-heptane and $Ca(DEHP)_2$ organic solution. The precipitates formed were filtered, washed with absolute ethanol [7].

Xinyu Song et al. developed a novel method for the controlling the $CaSO_4$ growth in organic media. The Ca^{2+} and SO_4^{2-} were taken out from the different extractants in the organic media. By changing the molar ratio of Ca^{2+} and SO_4^{2-} in the organic media calcium sulfate with different morphologies and size including nanoparticles, nano sheets and long fibers were prepared at room temperature. The effects of molar ratio of Ca2+ and SO42- on the CaSO4 growth were investigated. Research investigated that extractant primary amine and $DEPH^-$ were capable to suppress the growth rate of $CaSO_4$ in organic media. By changing the molar ratio of Ca^{2+} and SO_4^{2-} and organic solvent, different morphologies and sizes of the $CaSO_4$ crystals were controlled effectively. Compared with different sizes of crystals obtained at different conditions it was found that molar ratio of $[Ca^{2+}]$ / $[SO_4^{2-}] = 1$, was effective for inhibition of growth rate of crystals [7].

2.2 Microwave assisted method

The overall description of the method is as follows; calcium dodecyl sulfate was prepared by mixing $CaCl_2$ and saturated solution of sodium dodecyl sulfate (SDS). The precipitates formed were collected by centrifugation, washed with deionized water and dried in vacuum at 60 °C. Microwave oven was used for thermal transformation of calcium dodecyl sulfate to calcium sulfate nanowires [23-25].

Liang Li et al. reported a microwave assisted route for the preparation of calcium sulfate hemihydrate nanowires by using calcium dodecyl sulfate (CSD) as a precursors. The effect of different organic solvent namely ethylene glycol (EG), N, N-dimethylformamide (DMF) were investigated on the morphology and size of calcium sulfate nanowires. Also the relationship between heating method and reaction time were investigated.

Research results revealed that microwave assisted method didn’t require any seed or template for the preparation of calcium sulfate nanowires and different organic solvent had a little effect on the morphology of calcium sulfate nanowires. Nanowires of the different samples had an average diameter of 130 nm, length up to 30 µm and aspect ratio of about 62. Microwave heating also reduced the reaction time for the formation of calcium sulfate hemihydrate nanowires as compared to oil heating method [26].

2.3 Ultrasound-Assisted Method

Chinmay Hazra et al. unfold the ultrasound assisted/bio surfactant templated route for the synthesis of calcium sulfate α-hemihydrate with controllable morphology.

The overall procedure is as follows; the anionic biosurfactants i.e. rhamnolipids and surfactin were isolated and purified from Pseudomonas aeruginosa and Bacillus claussi respectively, as reported in [27, 28]. For the synthesis process 100ml beaker was used with constant rate of 250 rpm. The temperature of the solution was kept constant at ambient temperature. In situ deposition technique was used for synthesis of nanosized $CaSO_4$. Briefly, $CaCl_2$ (0.1M) was added into 100 ml distilled water. For experimentation the biosurfactants was transferred into the calcium solution before mixing with the sulfate solution. Biosurfactants was added in variable quantity in the aqueous calcium solution having a rhamnolipid/H_2O or surfactin/H_2O mass ratio ranging from 1.3-4.5 (step 1 solution). Aqueous calcium solution containing biosurfactants was exposed to irradiation for 10 min then it was transferred to the ultrasonic reactor. Another solution of $(NH_4)_2SO_4$ (0.1M) was put into step 1 solution and ultrasound irradiation was generated with a high intensity ultrasonic processor for 1.0 h to procedure CaSO4 particles. During sonication the temperature was kept constant at 30 °C by using ice bath so the external temperature had no effect on the reaction. The solid product obtained was washed with distilled water four times, rinsed with acetone and dried at 60 °C for 2 hours [29-31].

Process study showed that biosurfactants namely rhamnolipid and surfactin can be used to suppress the precipitation of calcium sulfate but in doing so the biosurfactants generate metastable phase which is very stable at room temperature. The main advantage of using cavitation, produced due to ultrasonic irradiation, is improved crystallization habit (crystal shape and l/w ratio) of the nano-$CaSO_4$, lesser amount of energy consumption, reduced process time and operation at ambient conditions[29].

2.4 Microemmulsion method

Briefly in the microemmulsion method, two reactants (say A and B) are introduced in two identical microemmulsion. Upon mixing of two reactants, the droplets collide and exchange the reactants. The small droplets serve as micro/nano reactors where the reaction occurs. Many variations in this procedure have been employed. For instance, one of the reactants can be placed in the solution into the microemmulsion containing the other reactant or can be added directly to microemmulsion as solid, liquid or gas. Use of two identical microemmulsion containing reactants is the most commonly used method of synthesis [32].

Bao Kong et al. established a reverse microemmulsion method of water n-hexanol for the synthesis of α-calcium sulfate hemihydrate submicron rods. They designated the water/n-hexanol/ cetyltrimethylammonium bromide (CTAB) system and studied the parameters like temperature, ratio of H_2SO_4/ $CaCl_2$, and CTAB/ water and reaction time were investigated to determine the domain of α-HH synthesis.

Experimental results revealed that increased molar ratio of H_2SO_4/ $CaCl_2$ favored the formation of HH in the product, so higher concentration of H_2SO_4 promoted precipitation of HH form the microemmulsion. Synthesis reactions were carried out at temperature of 80-95 °C. Lower temperature (80 °C) favored the formation of dihydrate while Hemihydrates were formed higher temperature (95 °C). In microemmulsion the ratio of surfactant to water is always critical that affects the droplet size and microemmulsion dynamics [33, 34]. Higher CTAB/water ratio favored the formation of α-HH even at lower temperature range. Calcium sulfate α-HH is metastable form of calcium sulfate. When it precipitates out of the solution it tends hydrate or dehydrates [20]. Reaction time controls the formation of α-HH from the solution. Carefully controlling the reaction time α-HH can be precipitated from the solution [35].

Z. Yates et al. synthesized the HH by microemmulsion method and investigated the effects on morphologies and aspect ratio. The morphology of the HH was controlled successfully over wide range of size using microemmulsion of water, n-hexanol and SDS [36]

2.5 Autoclave Method

The general procedure of the hydrothermal process is as follows; the calcium sulfate dihydrate formed either by natural gypsum or by mixing calcium chloride and sodium sulfate and are put into the autoclave at a temperature of 104 ^{o}C and at a pressure of 40 lb/in.^{2} for about an hour. The product was separated by the filter paper, washed with distilled water and dried in the oven at 105 oC for 2 hours [37-39].

E. C. COMBE and D. C. SMITH developed a hydrothermal method for the synthesis of calcium sulfate hemihydrate. As a first stage of process development they investigated the process variable in the dehydration of gypsum. The methods to treat the gypsum to confirm the reproducibility of the particle size and removal of other hydrates of calcium sulfate from the prepared material i.e. hemihydrate were investigated.

The results revealed that in dehydration process, no correlation was found between setting time and water content of the sample. The differences in shape were due to the differences in the impurities in the raw materials or physical characteristics of the gypsum or thermal history of the material. As the crystals of hemihydrate formed were larger size than the gypsum used for their preparation so in hydrothermal process crystal growth occurs in addition of the reaction. Method for the preparation of calcium sulfate HH was successfully developed [37].

Kangbi Luo et al. investigated the influence of temperature and solution composition on the formation of calcium sulfate whiskers. Calcium sulfate whiskers were prepared by mixing sodium sulfate and calcium chloride by co-precipitation method followed by hydrothermal treatment of the resulting precursors.

Experimental results indicated that the morphology and structure of the product were associated with the hydrothermal reaction temperature. $CaSO_4.2H_2O$ plates were formed at temperature of 100 ^{o}C, $CaSO_4.0.5H_2O$ whiskers were formed at 130-160 ^{o}C and $CaSO_4$ bars were formed at $\geq$ 170 ^{o}C. Water is more favorable for the growth of hydrothermal $CaSO_4.0.5H_2O$ whiskers as compared to NaCl solution [39].

Zongyou Pan et al. prepared the calcium sulfate whiskers by hydrothermal process and investigated the effect of ethanol as an additive. Calcium sulfate dihydrate (CSD) were prepared by the reaction of Ca(OH)2 and H2SO4 by using precipitation method. Ethanol was used as a morphology modifier. Then CSD were treated by hydrothermal method to produce the α-Hemihydrate.

Results showed that addition of ethanol directed to the fast preparation of CSD and high yield of CSD. The resulting calcium sulfate HH has uniform morphology and particle size. The addition of ethanol decreased the water activity in the reaction and led to larger supersaturation of ions in the solution during the CSD precipitation [40].

Qing Han et al. synthesized the calcium sulfate hemihydrate whiskers by co precipitation-hydrothermal method and investigated the influence of disodium hydrogen phosphate dodecahydrate ($Na_2HPO_4 \cdot 12H_2O$) on conversion of $CaSO_4.2H_2O$ to $CaSO_4.0.5H_2O$. The experimental procedure was slightly modified. After mixing of $CaSO_4$ and Na_2SO_4 by co-precipitation method, the resulting precipitates were filtered, washed and dried at 45 oC for 4.0 h. Then $Na_2HPO_4 \cdot 12H_2O$ and $CaSO_4.2H_2O$ were mixed with water to form the slurry containing 3-10 wt. % $CaSO_4.2H_2O$ and 0-8.72* $10^{\wedge -3}$ mol/L $Na_2HPO_4 \cdot 12H_2O$. Then this slurry was put in the autoclave and put it at 110-150 oC for 3 h.

Research results revealed that small amount of $Na_2HPO_4 \cdot 12H_2O$ influenced the formation of $CaSO_4.0.5H_2O$ whiskers. Small amount of Ca_3 (PO_4) was also produced in the conversion of $CaSO_4.2H_2O$ to $CaSO_4.0.5H_2O$. This enhanced the dissolution of $CaSO_4.2H_2O$, led to the increase of super-saturation for the formation of $CaSO_4.0.5H_2O$. The $CaSO_4.0.5H_2O$ produced had a thinner diameters and shorter lengths as compared to the blank experiment in which $Na_2HPO_4 \cdot 12H_2O$ was not used. Presence of $Na_2HPO_4 \cdot 12H_2O$ in small amount decreased the diameter from 1.0-10.0 µm to 0.5-2.0 µm and length from 70-300 µm to 50-200 µm [38].

S. C. Hou et al. developed the facile calcination-hydration hydrothermal reaction method (a modified hydrothermal method) for the synthesis of active $CaSO_4.2H_2O$ precursors form commercial gypsum and then to produce $CaSO_4.0.5H_2O$ with high aspect ratio. The gypsum was sintered at 150 ^oC for 3-6 h, and then it was mixed with water at room temperature for 1.0 h. The suspension was then treated in an autoclave at 135 ^oC for 4.0 h. After hydrothermal treatment the suspension was filtered and dried at 105 ^oC for 6.0 h. The influence of calcination and hydration on the morphology and structure of $CaSO_4.2H_2O$ and $CaSO_4.0.5H_2O$ was considered. Experimental results uncovered that active $CaSO_4.2H_2O$ precursors upgraded the morphology of the $CaSO_4.0.5H_2O$ whiskers. Active $CaSO_4.2H_2O$ also favored the hydrothermal dissolution of $CaSO_4.2H_2O$ and the formation of active $CaSO_4.0.5H_2O$ whiskers with high aspect ratio [39, 41].

Hua He et al. prepared the phosphogypsum (PG) based $CaSO_4.0.5H_2O$ whiskers by hydrothermal method in the presence of glycerol. The Effect and mechanism of glycerol were investigated on the preparation of $CaSO_4.0.5H_2O$ whiskers providing clue for the industrial application.

Firstly the PG was put into the autoclave having inner volume of 50 cm^3 and then water was added. After that glycerol in different percentages (with vol% 10, 20, 30, 40, 50, 60, 70, 80, 90, 100%) was added and treated at 140 oC for 2.0 h. After cooling down the autoclave naturally, samples were filtered, washed and dried at 100 ^oC for 5.0 h. Experimental results discovered that PG-based $CaSO_4.0.5H_2O$ whiskers were prepared successfully in the presence of glycerol by hydrothermal method. The optimal glycerol/ water volume ratio was 50%. Glycerol played major role in the dissolution of $CaSO_4.2H_2O$ and controlling the growth of $CaSO_4.0.5H_2O$ whiskers. The investigation on the formation mechanism of PG-based $CaSO_4.0.5H_2O$ whiskers by hydrothermal method on thermodynamic grounds might be favorable for the synthesis of inorganic crystals with particular morphologies, through controlling the growing crystals [42].

K. B. Luo et al. investigated the effect of additives (NaCl, $CaCl_2$, and Na2SO4) by preparing the CSWs by hydrothermal method. By the addition of additives the supersaturation of the solution increased which suppressed the growth of CSWs and also decreased the aspect ratio of whiskers. In the absence of additives the whiskers formed had a better morphology and higher aspect ratio [43, 44].

Xiao Wang et al. investigated the influence of solution composition on the morphology of CSWs prepared from flue gas desulfurization (FDG) gypsum in H_2SO_4-NaCl-H_2O system by hydrothermal method. Results revealed that as compared to the pure water the H_2SO_4-NaCl-H_2O system is more favorable for growth of CSWs. CSWs with the desired morphology can be prepared by controlling the composition of solution [45].

3. Conclusion

It can be concluded that calcium sulfate whiskers CSWs are important family of inorganic materials and new CSWs based materials are certainly among the most promising challenges in polymer composite materials in near future. The hydrothermal method is a most suitable one for the production of CSWs with controlled morphology and high aspect ratio. The research efforts should be continue for it advancement.

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Synthesis of Calcium Sulfate Whiskers from the Waste Calcium Chloride by Hydrothermal Proces

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Abstract— *Environment friendly, cost effective, non-toxic and thermally stable calcium sulfate whiskers have gained much attention as they are being extensively used as reinforcing or filler material in rubber, plastics, paper making, cement and composite materials. Previously the calcium sulfate whiskers were prepared either from gypsum by calcination or by the reactive crystallization of lime with sulfuric acid. This work focus on preparation of calcium sulfate whiskers by co-precipitation of sodium sulfate and waste calcium chloride discharged from the soda ash plant, followed by hydrothermal treatment of the precursors formed. The study of different process parameters i.e. reaction temperature, molar ratio of reactants, reaction time, mixing methods of reactants and stirring speed were carried out and conditions were optimized for production of calcium sulfate whiskers. Based on these conditions calcium sulfate whiskers with aspect ratio 15 were produced using sodium sulfate and waste calcium chloride. The experimental results revealed that calcium sulfate hemihydrate with an average length of 200 µm and width of 4-10 µm were produced by hydrothermal treatment using calcium sulfate dihydrate as precursors that were formed by co-precipitation of sodium sulfate solution into calcium chloride solution at 30 ^{o}C, at molar ratio of sodium sulfate to calcium chloride 0.5:1, reaction time of one & half hour and stirring speed of 150-250 rpm. The morphology of whiskers was examined with the field emission scanning electron microscope (SEM). The structures were identified by powder X-ray diffractometer (XRD). SEM results show good morphology of the whiskers and XRD provided phase identification. Results indicate that calcium sulfate whiskers can be prepared using waste calcium chloride from the Solvay process. Process study provides sound information for the utilization of $CaSO_4$ whiskers formed from waste calcium chloride as a reinforcing material in rubber, plastic, paper making and polymer composite materials. Also the price of calcium sulfate whiskers prepared by this process is very low that make them suitable for their use as reinforcing/ filler material. Process under consideration will provide an optimum utilization of calcium chloride which is a waste product of Solvay process.*

Keywords — Calcium sulfate, Whiskers, Solvay process, Waste $CaCl_2$ utilization, Hydrothermal synthesis

I. Introduction

Calcium sulfate whiskers (CSWs) are the fiber shaped single crystals having large length to diameter ratio. As a strengthening material, inorganic whiskers have drawn considerable interest as they have high strength and toughness. calcium sulfate whiskers (CSWs) are nearly free from internal defects as they have small diameter [1]. In recent years the CSWs, as a kind of environment friendly materials has been drawing much attentions as they are being used as filler/reinforcing material in rubber, plastic, paper making and polymer composite materials [2-5] owing to their thermal stability, resistance to chemicals and high tensile strength [6-8]. CSWs are low in price as compared to other inorganic whiskers for example CSWs are only 1/200~1/300 of the cost of silicon carbide (SiC) [9].

Methods have been developed for the synthesis of calcium sulfate whiskers, including the salt-solution method, reactive crystallization method, hydrothermal route, acidic amalgamation route and facile calcination of gypsum [10-14]. The hydrothermal route is more favorable due to uniformity in morphology of the product, moderate conditions and changeable process parameters [14, 15].

This work examines the probability of preparing calcium sulfate whiskers by co-precipitation followed by hydrothermal treatment, using sodium sulfate (Na_2SO_4) and the calcium chloride ($CaCl_2$) discharged from the Solvay process. In Solvay process, sodium carbonate ($NaCO_3$) is produced while producing $CaCl_2$ as a byproduct. A large amount of $CaCl_2$ is discharged each day during the production of $NaCO_3$, so it is difficult to handle this huge amount of waste. The $CaCl_2$ produced is either discharged into the rivers, lakes or is dumped on open land sites so it causes environmental issues. By using this waste byproduct natural resources can be saved and environment can be protected.

In this work, the study of different process parameters i.e. reaction temperature, molar ratio of reactants, reaction time, mixing methods of reactants and stirring speed were carried out and conditions were optimized for production of calcium sulfate whiskers from sodium sulfate and the calcium chloride discharged from ICI Soda Ash Plant, a sodium carbonate production plant.

The uniqueness of this work is that calcium sulfate whiskers have been synthesized by hydrothermal route by using waste calcium chloride discharged from the local ICI plant producing soda ash. Process under consideration has provided an optimum utilization of calcium chloride which is byproduct of Solvay process.

II. Experimental

Experimental procedure: Commercial grade Na_2SO_4 and waste $CaCl_2$ from the Soda Ash Plant were used for the experiment. 0.5-1.5 mol. L^{-1} Na_2SO_4 was mixed with 0.5-1.5 mol. L^{-1} $CaCl_2$ at varying temperature by dropping Na_2SO_4 solution to $CaCl_2$ solution and vice versa. The stirring speed was kept at (100-250 rpm) and dripping rate of 3 $mL.min^{-1}$. After the mixing of raw materials, the suspension was stirred for 1 h, then it was put into a small stainless steel autoclave that had an inner volume of 50 ml, heated (3 $^{o}C.min^{-1}$) to 120-150 ^{o}C and kept in isothermal conditions for 1.0-4.0 h. After this, the product was cooled down to room temperature naturally, filtered, washed with distilled water and put in oven for drying at 105 ^{o}C for 2 h.

A. Characterization

Scanning electron microscope (FESEM, JSM-6490LA, JEOL, JAPAN) was used to observe the morphology of the hydrothermal product. The composition of the product was analyzed by X-ray powder diffractometer (STOE XRD).

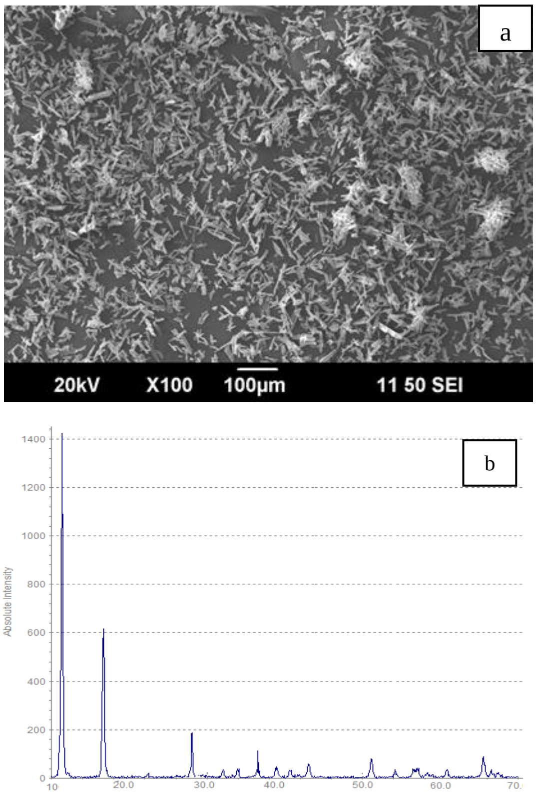

Fig. **1** Morphology (a) and XRD pattern (b) of the precursors formed at 30 ^{o}C.

III. RESULTS AND DISCUSSION

A. Characterization of precursors

Figure 1 exhibits the morphology and XRD pattern of the precursors developed at a temperature of 30 ^{o}C. The precursors were composed of irregular shape plates. The XRD results revealed that the precursors were formed of calcium sulfate dihydrate ($CaSO_4.2H_2O$).

B. Effect of Temperature on CSWs

Figure 2 shows the morphology of the calcium sulfate whiskers formed at different temperatures (30 ^{o}C, 55 ^{o}C and 85 ^{o}C) by adding Na_2SO_4 to $CaCl_2$ in solution form. The morphology of calcium sulfate whiskers, the hydrothermal product is connected closely with the temperature at which the precursors were formed. The increase of temperature leads to increase of precursor's size and hydrothermal product became more non-uniform and thicker as the temperature increased from 30 ^{o}C to 85 ^{o}C. The whiskers formed at 30 ^{o}C had length of 200 µm and diameter of 4-10 µm. The variation of morphology with the temperature can be explained on the basis of supersaturation at varying temperatures. Super-saturation (S) in equation form can be written as:

$$S = \frac{\left[Ca^{2+}\right]\left[SO_4^{2-}\right]}{K_{sp}} \qquad (1)$$

Where S is the supersaturation, K_{sp} is the equilibrium constant which was calculated out from the HSC software [16] and $[Ca^{2+}]$ and $[SO_4^{2-}]$ are concentration of the soluble Ca^{2+} and SO_4^{2-} respectively.

It is examined from table 1 that by increasing the temperature, the K_{sp} value of $CaSO_4.2H_2O$ decreased. Hence, the supersaturation at low temperature is small as compared to high temperature. Super-saturation is associated with growth rate of the crystals as stated in crystallinity theory. The more supersaturation, greater the growth rate of the crystals. Formation of $CaSO_4.2H_2O$ precursors is linked directly with the growth rate of the crystals. Low temperature favored the small growth rate so the precursors with smaller size were formed and hydrothermal product with uniform shape was formed. So the temperature 30 ^{o}C is favorable for the formation of precursors to form uniform hydrothermal product as compared to 55 ^{o}C and 85 ^{o}C.

TABLE I. EFFECT OF TEMPERATURE ON SUPERSATURATION

Temperature ^{o}C	**K_{sp}**	**S**
30	$3.10 * 10^{-5}$	201.5
55	$2.35 * 10^{-5}$	270.4
85	$1.42 * 10^{-5}$	441.6

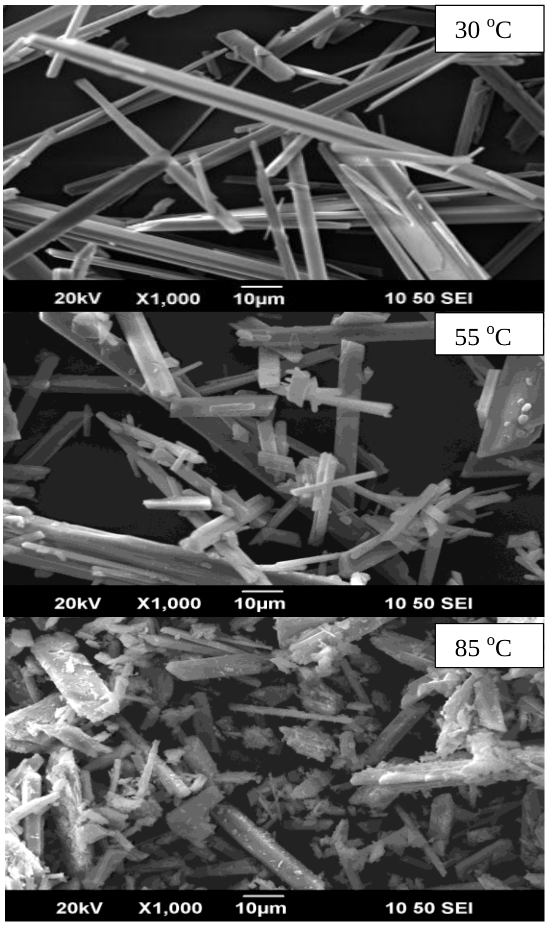

Fig. 2 Effect of temperature on hydrothermal product

C. Effect of mixing ways of Na_2SO_4 *and* $CaCl_2$

To examine the effect of mixing methods, the reactants at 30 °C were mixed in solution form by adding Na_2SO_4 to $CaCl_2$ and vice versa. Figure 4 shows the morphology of calcium sulfate whiskers, the hydrothermal product.

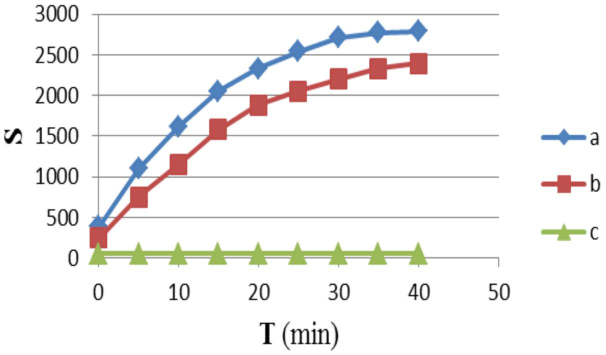

Fig. 3 Influence of the mixing ways of reactants on the super-saturation (a) $CaCl_2$ to Na_2SO_4 (b) Na_2SO_4 to $CaCl_2$ (c) K_{sp} of calcium sulfate dihydrate

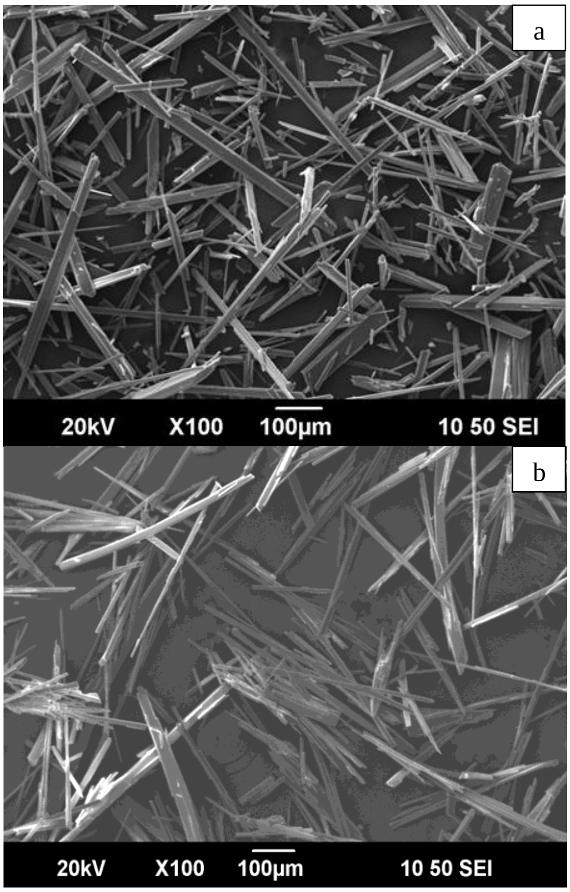

Fig. 4 Effect of mixing ways of the reactants, (a) Na_2SO_4 to $CaCl_2$ (b) $CaCl_2$ to Na_2SO_4

The mixing ways of reactants has a direct effect on the size of precursors and the morphology of the hydrothermal product formed. By adding the Na_2SO_4 to $CaCl_2$ the precursors with small size were formed and the hydrothermal product with large aspect ratio was formed while addition of $CaCl_2$ to Na_2SO_4 favored the precursors with larger size and hydrothermal products with small aspect ratio and irregular shape were formed. In figure 3 the S and K_{sp} are plotted against time which shows that the values of supersaturation are greater than K_{sp} which promote crystal growth. It is also shown that values for line ‘a’ are greater than that of line ‘b’, so supersaturation for the line a is superior than line b and the precursors size is also bigger for line ‘a’ as compared to line ‘b’. So supersaturation has a direct effect on the particle size of the precursors. For the formation of calcium sulfate whiskers with high aspect ratio, adding Na_2SO_4 to $CaCl_2$ is more favorable way as compared to $CaCl_2$ to Na_2SO_4 to mix the reactants.

D. Effect of molar ratio of the reactants:

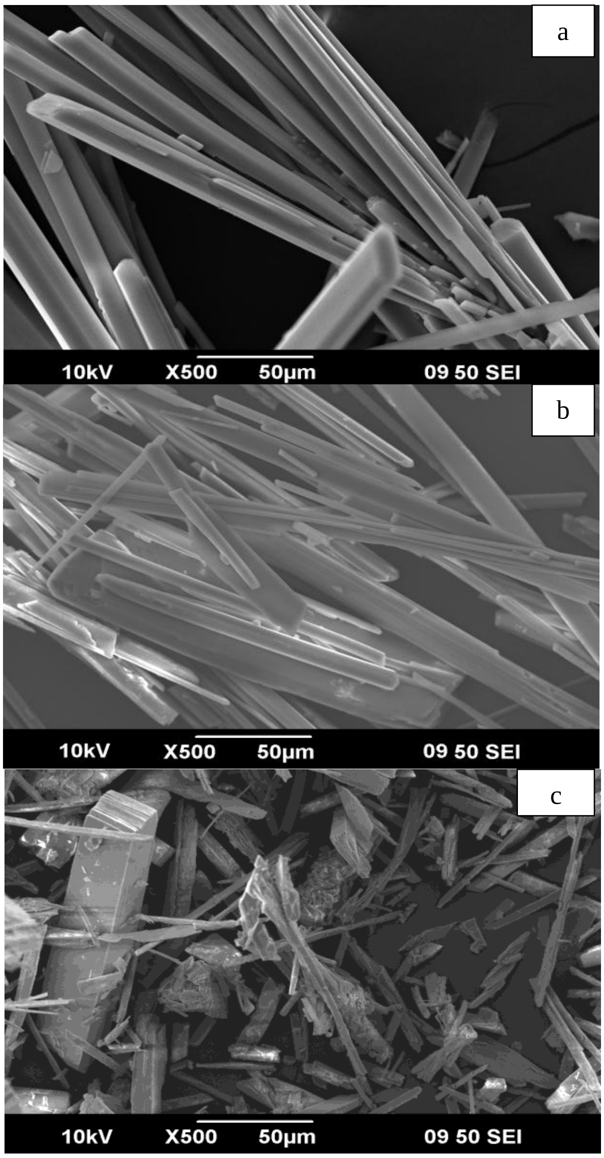

Fig. 5. Effect of molar ratio of reactants: Molar ratio of Na_2SO_4 to $CaCl_2$ (a) 0.5:1 (b) 1:1 (c) 1:0.5

To inspect the effect of molar ratio, the reactants in solution form were mixed by adding Na_2SO_4 to $CaCl_2$ at 30 °C and in molar ratio of 1:1, 0.5:1, and 1:0.5 to prepare precursors. After hydrothermal treatment the hydrothermal products were obtained. The SEM results are shown in the figure 5.

Low molar ratio of Na_2SO_4 to $CaCl_2$ was favorable for the development of hydrothermal product with high aspect ratio. Molar ratio being 0.5:1 of Na_2SO_4 to $CaCl_2$ resulted in formation of calcium sulfate whiskers having high aspect ratio. By comparing the data for supersaturation and $[Ca^{2+}]$ / $[SO_4^{2-}]$ with reaction time in case of molar ratios 1:1, 0.5:1, and 1:0.5, the supersaturation was smaller while the values of $[Ca^{2+}]$ / $[SO_4^{2-}]$ were larger in case of molar ratio of 0.5:1. So the precursors with smaller size were formed which favored the formation of hydrothermal product with high aspect ratio.

IV. Conclusion

Calcium sulfate whiskers were formed by co-precipitation of Na_2SO_4 and waste $CaCl_2$ at room temperature followed by hydrothermal treatment of the precursors formed. The parameters like reaction temperature, molar ratio of reactants, reaction time and ways of mixing the reactants influenced the size of the precursors and aspect ratio of corresponding hydrothermal product. The optimal conditions for the formation of precursors with small size and corresponding hydrothermal product with high aspect are: reaction temperature of 30 °C, reaction time of 1 & half hour, by mixing Na_2SO_4 to $CaCl_2$ in molar ratio of 0.5:1 and stirring speed 150-250 rpm. Process study provides reasonable utilization of $CaCl_2$ discharged from the Solvay process.

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