Chapter 1

Introduction

1.1 Importance of reusing industrial wastes

Rapid industrialization has uplifted the rate of urbanization from traditionally rural economies to modern sophisticated ones. Although it is a sign of development, it is imperative to note that our society is facing a grave ecological situation as a result of the large quantities of toxic industrial wastes generated on a daily basis due to this development. In India, nearly 250 million tonnes of industrial wastes was generated annually in the early 2000's [139] and that amount has been continuously increasing since then. Needless to say, the adverse impact of these industrial wastes on the environment is tremendous and cannot be ignored at all. Industrial wastes in the form of sludges and slags generated every day from various industries contain varying amounts of valuable metals, non-metals, compounds and materials which get disposed off into the environment. Although it is usually possible to recover these materials from the industrial wastes through various technologies and processes, it is often an uneconomical, expensive and tedious process to recover these products. Hence, they are disposed off in to the environment creating soil, water and air pollution in our society - an action which has become a cause of grave concern for posterity. Thus, it is imperative to mention that transformation of these solid wastes into something reusable by the parent industry or by different enterprises in varied domains is paramount for conservation of the important compounds or materials, and more importantly, for protecting the environment. Various steps in the direction of recycling and reusing industrial wastes have been taken in the last few years in order to mitigate this environment hazard. Industrial wastes such as phospho-gypsum, fly ash, copper tailings, petroleum effluent treatment plant (ETP) sludge, mine waste etc were reused in the production of bricks and construction materials [30], solid mineral waste were reused in making ceramic structural products; mine wastes used in road construction and building materials [275]; waste materials were reused in the fabrication of glass-based products [59]; natural fibres were recycled in polymer composites [42]; fibres from distiller's dried grains with solubles (DDGS) and corn grains were reused as fillers in polymeric composites [183]; recycled wood fibre based HDPE and polylactic acid composites are developed [26]; bean pod filled kaolin reinforced epoxy composites were developed for better sustainability with enhanced properties [121], enhancement in the properties of concrete and styrene-butadiene rubber respectively filled with glass fibre reinforced plastic waste powder [15, 18] and so on. Needless to say, recycling and reuse of industrial waste is one of the most important step to be taken by today's society and industry, which is paramount in providing a safe and clean environment for future generations.

1.2 Industrial lime sludge waste and its reuse

With the advent of industrial development, more and more industries are being set up, which also brings with it large quantities of toxic industrial wastes generated on a daily basis. As huge industries manufacturing paper, fertilizer, sugar, carbide, and soda ash cater to society's demand, they also generate a potentially hazardous waste material called lime sludge. Industrial lime sludge waste mainly consists of lime as calcium carbonate ($CaCO_3$) which on heating provides a chemical composition of 40-50 % CaO, along with small amounts of Al_2O_3, SiO_2, Fe_2O_3 and traces of alkali oxides after a loss on ignition (LOI) of 35-40 % [2]. This implies that almost all of lime sludge consists of calcium carbonate and some other ceramic oxides (small amounts Al_2O_3 and SiO_2). As per the report of the Central Pollution Control Board (Govt. of India), almost 4.5 million tonnes of lime sludge is produced from the paper, fertilizer, sugar, carbide and soda ash industries in India yearly [2]. This is usually disposed off in open or closed dumpyards or used in unscientific land filling which is potentially hazardous for the environment as it may cause

- Air pollution (sludge becomes powdery on drying, foul-smelling odour)
- Water pollution (leaching during rain or near water bodies, contamination of ground water) and
- Soil pollution (poor quality of soil, excess contaminants in soil, lack of aesthetics and scar on terrain)

However, triggered by the urgent need to develop environmental friendly waste utilization methods, some unconventional methods of lime sludge waste utilization have been developed over the years, such as, recovery of raw materials from sludge, production of bricks, ceramics and building materials from sludge, sludge pelletization for alternative fuel, feedstock for ethanol production, masonry construction, and even as potential fertilizers and composts [10, 73, 240, 254, 262]. Although various alternative applications of lime sludge has been proposed over the years, yet the reuse of this waste industrially and commercially has been limited to a few sectors such as the cement industry which uses lime sludge as a filler in cement production. This has resulted in the illogical dumping of lime sludge in and around industrial premises as well as societal areas, creating an environmental hazard for the entire eco system. Hence, it is paramount that a novel process is taken up in order to reuse the industrial lime sludge waste generated by the industries either by the parent industry or by some other organizations; in a bid to mitigate this environmental issue.

1.3 Use of industrial wastes in polymeric composites

Composites are structurally designed or in some cases, naturally occurring materials consisting of two or more materials with significantly different physical or chemical properties, but they retain their distinct as well as separate identities at both the microscopic and macroscopic scale in its final structure. The basic components of a composite material are the matrix and reinforcements, the individual properties of which play a significant function in the constitution of any composite. Therefore, when constituents of considerably dissimilar specifications are brought into a matrix, they considerably enhance one or even other properties of the new composite material. The biggest advantage of a composite material is that their properties can be tailored *i.e.* one can design the desired properties in the material. A composite material can be designed to provide the properties that exactly meets the requirements for a specific application by choosing the appropriate combination and content of reinforcing and matrix material. Based on their matrix materials, composite materials are categorized into three groups *i.e.* polymeric matrix composites, metal matrix composites and ceramic matrix composites. However, out of the three, polymeric matrix composites have proved to be the most abundantly used due to their diversity, low cost and design flexibility (ability to be molded into complex shapes) in addition to the usual advantages of composites such as high specific strength, light weight and economically affordable. Thus, polymers and polymeric composites constitute the building blocks of almost every item surrounding us due to their various inherent features such as lightweight, functional and structural flexibility, low cost, and ease of manufacturing, to name a few.

Polymeric composites are often supplemented with inorganic mineral fillers mainly to reduce the material cost. However, numerous researches over the years have shown that filler addition can also improve their mechanical, thermal, and electrical properties in addition to reducing the product cost; thus increasing their commercial viability and structural reliability [32, 80, 136, 286]. This has paved the way for the reuse of industrial wastes in polymeric composites as particulate or fibrous fillers due to their ability of enhancing the properties of the composites. This would extend the range of their applications in addition to mitigating the disadvantages of environmental pollution. Thus, numerous researches have been conducted till date to reuse various industrial wastes as fillers/reinforcing agents in polymeric composites, as a process of sustainable waste management. Industrial wastes *viz.* biochar [61], post consumer recycled wood [242], electronic wastes [243], non-metals recycled from waste printed circuit boards [270], Thal silica [9], industrial fly ash cenospheres [66], red mud wastes [196], discarded nylon carpets [182], cotton gin waste and flax fibers [25], etc., are being used as fillers or reinforcing agents in a polymeric matrix in order to increase their functionality and decrease pollution. Needless to say, using these wastes in polymeric composites have improved one or the other properties of the composites based on the combination of the constituents. Hence, it may be stated that addition of various industrial wastes in polymeric composites as reinforcing fillers provide for three folded advantages *i.e.* (i) lowers the cost of the composite due to the addition of cheap wastes, (ii) improves the properties of the composites increasing their commercial viability and structural reliability, and most importantly (iii) reuse an industrial waste thereby mitigating environmental pollution.

However, an important challenge of adding inorganic materials (including waste fillers) in a polymeric matrix is the low interfacial adhesion at the filler-matrix boundary which causes the filler particles to drop out of the matrix upon application of stress. This results in low mechanical properties in these composites as the efficiency of the matrix in transferring stress to the reinforcing agents upon loading is reduced to a great extent. Hence, either the reinforcing phase or the matrix is usually physically or chemically modified in order to enhance interfacial adhesion and thereby improve the mechanical properties of the composites. Chemical modification with agents such as alkaline, fatty acid (stearic acid), maleic anhydride, silanes, peroxide, etc [75] and physical modification with corona or plasma treatment [35, 75] are certain techniques that has been used in this domain in order to improve interfacial adhesion at the filler-matrix boundary. Nevertheless, it is imperative to mention that industrial waste are commercially used in composites primarily because they offer a cheaper option in terms of reinforcing phase in addition to other factors such as mitigating environmental pollution and improving composite properties. Thus, for an industrial waste to be an attractive option in terms of its commercial viability as a reinforcing filler in a composite, it has to be available at a lower cost, which calls for cheaper material and processing techniques. The various surface modification techniques implemented in order to improve composite properties, require extra additional costs in terms of chemicals, equipment and facilities. This makes the organization which is trying to reuse industrial wastes, hesitant about investing in such techniques irrespective of the fact that the composite properties are greatly enhanced upon using such modification processes. Hence, the interfacial modification process should be chosen such that it becomes an optimized model providing composites with the desired mechanical properties at reduced manufacturing cost which would make them commercially viable and structurally reliable.

Additionally, proper prediction of composite properties is equally important in order to avoid the rigors of experimentation as it is tedious and expensive. Thus, an effective way of reducing experimental complications is to develop robust mathematical models for predicting the reinforcing filler content in the polymeric matrix so that it provides the required composite parameters *viz.* process parameters, mechanical properties etc. Numerous attempts have been made over the years to develop and optimize mathematical models for accurate prediction of composite properties. Earlier, regression analysis were used in order to predict the properties related to glass fibre reinforced composites [108], wood - polymer composites [276], lignocellulosic filler-polyolefin bio-composites [268], dental composites [51], calcium carbonate impregnated coir-polyester composites [112] and so on. Thus, it has been found that a prediction model is paramount for proper estimation of composite properties without implementing the expensive and tedious rigors of experimentation.

1.4 Potential use of lime sludge as a filler in polymeric composites

It is evident that industrial lime sludge waste acts an environmental hazard causing pollution when disposed off via conventional means and that there is an urgent requirement to develop alternative low cost solutions for recycling or reusing lime sludge for the greater good of the society. Although various alternative solutions to reuse lime sludge have been suggested, these solutions have not been adopted in a large scale due to varied reasons such as higher cost, commercial infeasibility, product inefficacy and so on. This research aims at improving the commercial viability and ability of lime sludge by reusing industrial lime sludge waste as a reinforcing filler in polymeric composites. This would account for three advantages - composites with superior properties, low cost (since lime sludge waste is very cheap) and reduced environmental pollution. Exhaustive study of industrial lime sludge waste as filler in polymeric composites have not been conducted till date. This study would provide the knowhow on the feasibility of using lime sludge as a filler in terms of structural integrity as well as economical viability. To make the reuse of lime sludge cost efficient as well as mechanically effective, raw lime sludge is used as a filler in a polymeric matrix in this study whereby the mechanical, thermal and morphological properties of lime sludge filled polymeric composites are studied. Additionally, it is also clear that inorganic fillers in composites yield low mechanical properties due to low interfacial adhesion at the filler-matrix boundary. Hence, compatibilizers or surface modifiers are significant in modifying the filler-matrix interface, thereby enhancing the interfacial adhesion resulting in better mechanical properties. However, these compatibilizers must be chosen such that the fabrication process is inexpensive to be commercially feasible while at the same time it should also improve the composite properties significantly. Stearic acid helps in uniform dispersion of particles in the polymeric matrix as the tendency of the coated filler particles to agglomerate reduces substantially. Thus the study of stearic acid surface modified lime sludge waste filled polymeric composite would be interesting to understand the effect of a compatibilizer on the mechanical properties of the composites. Moreover, an industrial waste to be commercially attractive as a reinforcing filler, it must be versatile enough to improve properties of composites irrespective of the matrices and reinforcing agents that it is used along with. Therefore, the effect of lime sludge addition in different types of matrices or along with other reinforcing agents in composites also needs to be evaluated.

1.5 Outline of the thesis

The rest of the thesis is outlined as the following:

- **Chapter 2:** Includes a literature review intended to present an outline on the current knowledge environment already in existence, relating the issues of interest. This review emphasises on the current problems, recent developments and applications of particulate reinforced, fibre reinforced, multi component hybrid composites in engineering applications. Additionally, it also presents the research works proposed over the years on the use of industrial waste in polymeric composites and alternative uses of industrial lime sludge waste. Moreover, domains that need further investigation related to characterization and property behaviour of these composites are also identified.

- **Chapter 3:** Includes an account of the raw materials and experimental techniques employed. It details out the procedures by which composites are fabricated and lime sludge is coated with stearic acid. Moreover, description of the equipment and procedures used for characterization of the test specimens are also presented in this chapter.

- **Chapter 4:** Includes the mechanical, thermal, and morphological behaviour of raw industrial lime sludge waste filled HDPE composites. Mechanical characterization of the composites under tensile, flexural and impact loading is studied in conjunction with morphological behaviour in order to explain the behaviour of raw lime sludge filled composites under these conditions. Additionally, the thermal properties of these composites are also presented with the aid of characterization techniques such as DSC and TGA. Furthermore, a consolidate regression based model is established for the mechanical parameters as a function of lime sludge content.

- **Chapter 5:** Includes the effect of stearic acid coating of lime sludge particles on the mechanical, thermal, morphological and water absorption properties of stearic acid coated lime sludge filled HDPE composites. Since, particle agglomeration hinders effective reinforcing ability of raw lime sludge, hence the effect of stearic acid coated lime sludge particles on the properties of the composites is studied in comparison with that of raw lime sludge filled HDPE composites. Moreover, a consolidated regression based model is established for the mechanical parameters as a function of stearic acid coated lime sludge content are presented. The models developed for tensile parameters based on regression analysis are subsequently compared with popular theoretical models proposed over the years to obtain a more precise correlation between theoretical and experimental study.

- **Chapter 6:** Includes the effects of lime sludge filler in different types of hybrid composites in order to test the versatility of lime sludge as a filler/reinforcing agent in polymeric composites. Hence, the effects of lime sludge on the mechanical properties of a variety of lime sludge filled composites *viz.* HDPE-PP blends, HDPE-MAPE, coir-HDPE-MAPE, epoxy and coir-epoxy composites. The effect of varying the weight fractions of lime sludge, MAPE compatibilizer and coir on the properties of the composites are discussed in this chapter.

- **Chapter 7:** Includes a synopsis of the outcomes of this investigation along with the main conclusions drawn from the present study. Furthermore, it also contains suggestions and scope for future research work in this domain.