Abstract

Although advent of industrialization has made rapid technological developments in our daily lives, this increasing demand for industrial goods has also led to the generation of huge quantities of wastes at a speedy scale. Industrial waste generated are being dumped indiscriminately in dumpyards or in water bodies polluting air, water and land. Since there is no other alternative to the huge demand of goods and growth of industries, there is an urgent need to curb the materials produced as by products which are not eco-friendly, at least for the sake of posterity. One such industrial waste is lime sludge waste derived from the paper and pulp, carbide, soda ash and fertilizer industries which account for almost 4.5 million tonnes per annum in India itself. Lime sludge waste is generally disposed off in open or close dumpyards or used in indiscriminate land filling; thus polluting the environment nearby and posing as an environmental hazard in terms of human health issues. Lime sludge mainly consists of lime as calcium carbonate ($CaCO_3$) along with a few amounts of ceramic oxides. Although various alternative ways of lime sludge reuse has been proposed through various researches, yet the reuse of lime sludge commercially in various alternative applications has been far from successful. Even though recycle of lime sludge in the same industry from where it produced is possible, the process is uneconomical and hence, not practised by the industries themselves. Needless to say, an alternative application for reusing lime sludge waste which will be commercially attractive as well as an improvement over the existing alternative/application, is paramount for mitigating environmental pollution caused by lime sludge.

This thesis presents the idea of using industrial lime sludge waste as a filler in polymeric composites. It is usually common for manufacturers to add a filler in polymeric composites such that it is not too detrimental to the composite properties but reduces the cost of the product. However, common fillers such as $CaCO_3$ often improve certain properties like viscosity, rigidity, toughness etc. of the composites in addition to reducing the cost of the composite. In similar context, since lime sludge is a $CaCO_3$ based waste, it has the potential to be instrumental as an

effective reinforcing agent in polymeric composites. This would lead to production of composites with certain properties superior than the virgin polymer. Lime sludge addition in these polymeric composites as a filler would also provide an alternative way of reusing this industrial waste. This idea is in line with the various studies being carried out nowadays, on different types of wastes (both particulate and fibrous) being used as fillers/reinforcing agents in polymeric composites. It may be stated that lime sludge is an entirely inorganic material and is different from paper sludge (from the paper industry) in the sense that, paper sludge consists of about 30% organic matter in the form of cellulosic fibres. The organic matter in paper sludge offer certain disadvantages in the composite properties such as low interfacial bonding, lower thermal stability, higher water absorption rate and generation of high stress concentration sites in the composites (due to large particulate size of cellulosic fibres).

Hence, in the first phase of this research, raw lime sludge waste is used as a filler in high density polyethylene (HDPE) matrix and the mechanical, thermal and morphological properties of these composites are studied. It is found that addition of lime sludge particles in the polymeric matrix enhanced the stiffness (both tensile by 1.54 times and flexural by more than 2 times) while decreasing the tensile strength, ductility and impact toughness due to - (1) the rigidity provided by the lime sludge particles and (2) low interfacial adhesion at the filler-matrix boundary. Additionally, the flexural strength also increased by almost 2 times (from 6.23 MPa to 12.19 MPa) indicating better stress transfer between filler and matrix under bending stresses. Study of thermal properties showed that lime sludge is thermally stable even up to a temperature of 600 °C. Hence, thermal parameters such as the thermal stability, onset temperature of thermal degradation, melting temperature, melting enthalpy and residual weight percent (measured through thermogravimetric analysis) enhanced due to the addition of lime sludge particles in the composites. This study revealed that industrial lime sludge waste has the potential to be an effective filler in polymeric composites. Thus, reuse of lime sludge waste as filler in polymeric composites would enhance the functionality and commercial viability of both the filler and the polymer in addition to reducing the cost of the composite. Morphological study however, revealed low interfacial adhesion at the filler-matrix boundary and filler particle agglomeration (larger effective particle size) at higher filler concentration in the composites (leading to high stress concentration sites). This results in low tensile strength, ductility and impact toughness of the composites at higher filler content leading to this premature failure upon load application.

An important challenge of using inorganic raw lime sludge particulate fillers without any surface modification is that it produces composites with low strength (tensile and impact) due to unwanted particle agglomeration and low interfacial adhesion. Hence in the second phase of the research, stearic acid is used to surface modify the lime sludge particles before being used as filler in HDPE composites. Surface modifier such as stearic acid is cheaper and more widely available than its contemporary chemicals which makes it an attractive option in terms of its commercial viability. Inorganic mineral fillers are hydrophilic while organic polymers are hydrophobic in nature; this causes problems such as low interfacial adhesion. Moreover, homogenous dispersion of inorganic lime sludge particles in an organic polymer matrix is difficult due to the strong tendency of the particles to agglomerate and also generate high viscosity during composite processing. Stearic acid provides a monolayer of hydrophobic organic molecules on the filler surface which hinders particle agglomeration, by enhancing uniform particle dispersion in the matrix. Hence, properties of stearic acid coated lime sludge filled HDPE composites are studied in conjunction with virgin polymer and raw (uncoated) lime sludge filled composites in order to assess the effects of using a surface modifier on the properties of the composites. It is observed that the composites containing the modified lime sludge exhibited better strength (tensile, flexural, and impact) and ductility than uncoated composites. Tensile strength was found to be highest for 25 wt % lime sludge (15.08 MPa) for coated composites as compared to 10 wt % lime sludge (13.67 MPa) for uncoated composites. Flexural strength increased from 12.19 MPa to 12.50 MPa at 30 wt % lime sludge for coated composites; while the impact strength increased by 3 folds for coated composites when compared with raw lime sludge filled composites. Stearic acid coating hindered particle agglomeration (low stress concentration sites) and ensured uniform dispersion of filler particles in the matrix. However, the rigidity of the uncoated composites is found to be slightly higher than the coated counterparts owing to the higher mechanical restriction in chain mobility posed by the uncoated rigid lime sludge particles. Thermal studies showed that stearic acid coating increased entanglement at the filler-matrix interface leading to their decomposition to residual amounts, at a temperature 100 °C higher than the uncoated composites. Stearic acid coating also reduced the water absorption rate of composites by enhancing the wettability and dispersability of lime sludge particles in the matrix, thus reducing the effective surface area for water absorption. Hence, stearic acid proved to be an effective and cheap surface modifying agent for lime sludge as it hindered particle agglomeration and ensured uniform dispersion of particles in the matrix. This resulted in coated particulate composites displaying better properties than uncoated ones. Having said that, morphological studies revealed that the interfacial adhesion at the filler-matrix boundary is still not up to the mark due to low compatibility between filler particles and the matrix. Hence, better and expensive surface compatibilizer such as maleic anhydride grafted high density polyethylene (MAPE) may be used in order to ensure effective adhesion at the interface.

It is paramount that a structurally reliable and commercially feasible filler material must be versatile enough to be used in conjunction with a variety of matrices and reinforcing agents. Hence, the third aspect of this thesis deals with lime sludge being used as a filler in various hybrid composites *viz.* HDPE-MAPE, HDPE-PP blends, coir-HDPE-MAPE, epoxy, and coir-epoxy composites. This is done in order to assess the effects of lime sludge addition on the properties of different types of composites. The effect of lime sludge particles on different hybrid polymeric composites showed a similar trend in the overall mechanical behaviour of the composites as shown by coated and uncoated lime sludge filled HDPE composites. It is observed that lime sludge acts an effective reinforcing agent in all these composites up to a certain filler concentration under both tensile and bending loading conditions. Lime sludge also improved the rigidity of the composites by increasing the tensile and flexural modulus while decreasing the ductility of the composites. Moreover, MAPE is also used as the surface compatibilizer in these lime sludge filled composites to enhance adhesion at the filler-matrix boundary. It is observed that addition of 5 wt % MAPE as a compatibilizer proved to an effective agent in improving the filler-matrix interfacial adhesion, thereby improving the overall mechanical properties of the composites. Additionally, MAPE added lime sludge composites exhibited much superior properties than stearic acid coated and uncoated lime sludge-HDPE composites due to effective adhesion at the interfacial boundary. In case of lime sludge filled coir-epoxy hybrid composites, it is found that a 6 wt % lime sludge provided the best properties for the composites in case of both short and long coir fibre composites. Needless to say, lime sludge filled long coir fibre reinforced epoxy composites exhibited superior properties when compared with the short fibre composites. This is due to the ability of continuous fibres aligned in the direction of loading to withstand more stress than randomly dispersed short fibre reinforced composites. Moreover, lime sludge also increased the thermal stability of the composites by increasing the residual weight fraction left at 600 °C in lime sludge filled HDPE-PP blends and coir-epoxy composites.

Additionally, non linear regression models are developed for each mechanical properties as a function of lime sludge content for both stearic acid coated and uncoated lime sludge filled HDPE composites. It is found that the regression models formulated fitted satisfactorily with the experimental data. The regression models developed for tensile parameters are also compared with popular existing theoretical models in order to correlate the experimental results with theoretical models. It was found that the experimental data fitted well with certain theoretical models, which provided an insight into the nature of the composites.

It is imperative to state that exploring the feasibility of reusing industrial lime sludge waste as a reinforcing filler in polymeric composites is paramount for determining a commercially viable alternative application for lime sludge. This thesis discussed the effects of the lime sludge addition on the properties of various types of polymeric composites. It is found that lime sludge proved to be an effective reinforcing agent in polymeric composites which has paved the way for three types of advantages - (i) production of composites with superior properties, (ii) reduction in the cost of the composites (as lime sludge is a waste) and most importantly (iii) reuse of an environmentally hazardous waste for the benefit of the society.