A study of industrial lime sludge waste as filler in hybrid polymeric composites

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Abstract. Industrial lime sludge waste is an environmental hazard, which is usually disposed in dump yards causing pollution. This study aims to increase the viability of lime sludge (LS) by using it as filler in hybrid polymeric composites. Study of the mechanical properties of LS filled high density polyethylene (HDPE) and maleic anhydride grafted high density polyethylene (MAPE) revealed better properties of MAPE due to effective interfacial bonding at the filler-matrix boundary owing to the presence of maleic anhydride compatibilizer. LS also proved to be an effective reinforcing filler in case of short coir fibre - epoxy hybrid composites, thereby increasing their tensile strengths upon filler loading up to 9 wt %. LS improved thermal stability of the LS-coir-epoxy hybrid composites by increasing the thermal degradability and residual wt. %. However, it is observed that the addition of coir and LS in composites increased the water absorption rate of the composites significantly. Nevertheless, lime sludge proves to be an efficient filler in polymeric composites which would not only decrease pollution but also manufacturing cost of polymeric composites.

1.0. Introduction

Growing concerns regarding environmental safety has brought over a paradigm shift towards designing eco friendly materials and reusing/recycling hazardous wastes. Hence, over the past few years, natural fibres have drawn substantial interest from researchers as a potential replacement for synthetic fibres such as glass, aramid etc. in polymeric composites [1]. Among all natural fibres, coir is an important ligno-cellulosic fibre obtained from coconut trees grown extensively in tropical countries, like India [2]. General advantages of coir fibre include low density, low cost, high toughness, reasonable specific strength, recyclability, eco-friendly and biodegradability [1]. Hence, numerous researches on coir fibre based polymeric composites have been conducted till now. High strength and modulus properties of the coconut fibres have enabled its utilization in new composites for a broad range of applications such as building materials and household appliances, composite armouring design to resist the impact of explosions, wind mill blades, industrial shafts, fuel cylinders for natural gas vehicles, paper making rollers and even support beams of bridges [3].

On the other hand, a potentially hazardous industrial waste material is lime sludge (LS) produced primarily from paper, fertilizer, sugar, carbide and soda ash industries accounting for approximately 4.5 million tons per annum in India [4]. A substantial amount of lime sludge waste is disposed of unscientifically causing air, water and soil pollution. LS waste consists of calcium carbonate (CaCO₃) as the major constituent [4]. Currently, industrial wastes viz. biochar [5], post-consumer recycled wood [6], electronic wastes [7], modified steel slag [8], waste fibre reinforced polymer (FRP) and corn...
straw [9], industrial fly ash cenospheres [10], red mud wastes [11], artificial marble powder [12] etc., are being used as fillers or reinforcing agents in a polymeric matrix in order to increase their functionality and decrease pollution.

However, the main disadvantage of coir as reinforcement in polymer composites is unsatisfactory due to its high cellulose, hemicellulose and lignin content, and high micro-fibrillar angle. Hence, coir fibres are surface treated with an alkali in order remove the lignin on the surface, before using it in composites [13, 14]. Additionally, compatibilizers such as maleic anhydride, silanes etc. are used to increase the adhesion of fillers or fibres with the matrix.

Off late, a substantial amount of research on hybrid composites with a variety of filler-fibre combinations have been conducted viz. bio particles-coir [15], crab carapace-coir [16], powdered hazelnut shells-jute [17] etc. in various polymer matrices. This is done in order to reap the benefits of both the reinforcing agents. This research study intends to analyze the factors which have significant influence on properties of a hybrid lime sludge-coir fibre composite. In this study, effect of lime sludge waste and short coir fibre addition on polymeric composites is studied in order to reap the benefits of using an industrial waste and a natural fibre.

2.0. Methodology

2.1. Materials

HDPE grade 5108L, supplied by Haldia Petrochemicals Ltd. with a melt flow index of 1.9 g/min (@190°C, 2.16 kg) and density of 0.95 g/cm\(^3\) is used as the polymeric matrix. Maleic anhydride (MA) grafted HDPE (OPTIM E156) was obtained from Pluss Polymers Pvt. Ltd., Gurgaon (India). Raw lime sludge powder is collected from the dump yard of the Hindustan Paper Corporation Limited (HPCL) paper mill at Jagiroad, Assam (India). The lime sludge is ground and heated at 110°C for 2 hours to remove any residual moisture content in a hot air oven (model: 114/14, make: Reico) before blending. Coir fibre is obtained locally and is surface treated with 5% NaOH solution to remove any lignin from its surface. Epoxy (Lapox-12) and hardener are obtained from Perfect Trading Company, India.

2.2. Sample preparation

LS-HDPE and LS-MAPE composites with various weight % of LS (5, 15, and 25wt. %) are blended together in a co-rotating twin screw extruder (model: EX100, make: Voltam). Finally, the test specimens are molded, by using an injection molding machine (model: IM100, make: Voltam). The injection pressure is fixed at 2.45 N/mm\(^2\) and barrel temperature at 200°C during molding. LS-HDPE and LS-MAPE composites with 5, 15, and 25 wt. % LS are fabricated. Additionally, short (8 mm) coir fibre reinforced epoxy composites are filled with LS wt. % of 3, 6, 9 and 12 respectively are fabricated. Short coir fibres are randomly dispersed with a content of 30 wt. % in the composites and molded using a compression molding machine (make: SANTEC) at a compression pressure of 10 kg/cm\(^2\) for 24 hours.

2.3. Mechanical testing

The tensile and flexural properties are measured using a universal testing machine (model: H100K-S, make: Hounsfield) at a crosshead speed of 1 mm/min and using a 250 N load cell. The notched Izod impact test is conducted using a digital pendulum impact testing machine (model: P/N0963.000, make: CEAST Spa Italy). Tensile, flexure and impact testing of the composites are conducted according to ASTM D638 (specimen V), ASTM D7264 and ASTM D256 standards respectively. Three specimens for each composition of composites have been tested.

2.4. TGA analysis

The thermo-gravimetric analysis (TGA) is done by a Shimadzu, Japan thermo-gravimetric analyzer, TG50. Samples weighing about 6 mg each are heated from 25°C to 500°C in nitrogen at a flow rate of
30 ml/min with a heating rate of 10°C/min. TGA thermograms are plotted for 3 and 9 wt. % lime sludge added coir-epoxy composites.

2.5. Water absorption test

Water absorption (WA) properties are measured according to ASTM D570-98. The specimens are dried overnight at 70°C in an oven before undergoing the test. WA is calculated by weighing the specimens before and after immersion in distilled water at room temperature (25°C). The water absorption % is calculated using the equation 1.

\[
WA (\%) = \left[ \frac{W_a - W_b}{W_b} \right] \times 100
\]

Where \( W_a \) and \( W_b \) are the weights of the specimen before and after immersion respectively.

3.0. Results and discussions

3.1. Mechanical properties of LS-HDPE and LS-maleic anhydride grafted HDPE (MAPE) composites

Tensile, Flexural and impact testing of LS added pure HDPE and MAPE composites is carried out in order to study the effect of lime addition and maleic anhydride compatibilizer in the composites. Specimen samples are shown in Fig. 1 (a). The mechanical properties obtained for the composites are tabulated in Table 1. It is found that there is a moderate drop in the overall tensile strength with increasing filler loading for LS-HDPE composites when compared with pure HDPE. This is attributed to low bonding between the filler particles and the matrix leading filler-matrix interfacial dewetting under tensile loading. However, it is observed that the tensile strengths of LS-MAPE composites are higher than that of raw LS composites for all filler wt. %. Higher tensile strengths of LS-MAPE composites indicate better physical interaction at the filler-matrix interface due to the presence of maleic anhydride compatibilizer grafted on the HDPE chains. LS particles are hydrophilic in nature while the HDPE chains are hydrophobic which causes weak interfacial bonding between the filler and matrix. Maleic anhydride (MA) grafting modifies the interface, thus providing strong interfacial bonding and as a result, the increase in the tensile strength.

A significant increment in the elastic modulus of composites with increasing filler content (both LS-HDPE and LS-MAPE) is observed when compared with pure HDPE due to the replacement of a polymeric matrix with rigid particles, thus restricting the chain mobility hindering deformation within the elastic limit. Elastic modulus of MAPE composites are found to be higher than the raw LS composites due to the effective interfacial bonding between the filler and matrix.

Elongation at break decreased significantly with increasing filler content which is a characteristic of particulate reinforced composites. Low elongation of rigid filler particles, probable filler agglomeration at higher LS concentration (stress concentration sites) and dewetting along filler-matrix boundary (ineffective stress transfer from the matrix to the filler particles) are prime reasons for the decrease in the ductility of the composites. Since the dewetting is much lesser in MAPE composites, hence, better ductility is observed in these composites when compared with that of raw LS filled composites.

Increase in the flexural strength may also be attributed to high mechanical anchorage of the matrix provided by rough lime sludge particles and better stress transfer at the filler-matrix interface under bending stresses. Additionally, excess polymer on the surface as a result of the restriction imposed by the mold walls during molding of the composites lead to smooth composite surfaces which hinder generation of cracks at the surface of the specimen (at top and bottom surfaces) during bending. Better physical interaction and entanglement between LS particles and the MA modified HDPE chains under bending stresses lead to better flexural strengths for MAPE composites. Higher concentration of rigid particulate materials requires higher stress for the same amount of deformation and hence, increase in the flexural modulus is also observed for both types of composites.
Figure 1: (a) Tensile and flexural specimens for lime sludge – HDPE composites; (b) Tensile test and fractured samples of lime sludge-coir-Epoxy composite.

Table 1. Mechanical properties of LS - HDPE and LS – MAPE composites.

|                  | Tensile strength (MPa) | Tensile Modulus (MPa) | Elongation at break (%) | Flexural Strength (MPa) | Flexural Modulus (MPa) | Impact Strength (J/m) |
|------------------|------------------------|-----------------------|--------------------------|------------------------|-----------------------|-----------------------|
| Pure HDPE        | 16.88                  | 139.25                | 806.0                    | 6.23                   | 245.73                | 30.21                 |
| 5LS-95PE         | 11.91                  | 140.30                | 680.0                    | 8.48                   | 452.70                | 8.93                  |
| 15LS-85PE        | 11.96                  | 164.20                | 71.85                    | 10.03                  | 527.92                | 7.79                  |
| 25LS-75PE        | 11.24                  | 188.0                 | 39.48                    | 10.72                  | 599.5                 | 7.52                  |
| 5LS-95MAPE       | 16.94                  | 196.23                | 252.0                    | 13.64                  | 482.3                 | 31.79                 |
| 15LS-85MAPE      | 17.54                  | 219.20                | 68.20                    | 14.33                  | 556.0                 | 41.24                 |
| 25LS-75MAPE      | 18.59                  | 256.85                | 32.10                    | 15.14                  | 622.0                 | 44.34                 |

Table 2. Mechanical properties of LS - Epoxy and LS – Short Coir fibre (8mm, 30 wt. %) - Epoxy composites.

|                  | Tensile strength (MPa) | Tensile Modulus (MPa) | Elongation at break (%) |
|------------------|------------------------|-----------------------|--------------------------|
| Pure Epoxy       | 3.72                   | 374.0                 | 5.02                     |
| 3LS-97 Epoxy     | 4.83                   | 400.0                 | 4.80                     |
| 6LS-94 Epoxy     | 8.45                   | 426.0                 | 4.61                     |
| 9LS-91 Epoxy     | 6.37                   | 456.0                 | 3.20                     |
| 12LS-88 Epoxy    | 3.68                   | 493.0                 | 2.06                     |
| 30 Coir - Epoxy (8mm) | 16.27                | 411.3                 | 10.14                    |
| 3LS -30 Coir - Epoxy (8mm) | 12.33                | 452.0                 | 9.18                     |
| 6LS - 30 Coir - Epoxy (8mm) | 16.19                | 496.0                 | 8.54                     |
| 9LS - 30 Coir - Epoxy (8mm) | 13.76                | 521.0                 | 6.74                     |
| 12LS -30 Coir - Epoxy (8mm) | 12.90                | 543.2                 | 6.17                     |

It is observed that the impact properties decreased with the introduction of LS particles as compared to the pure HDPE. Highly stiff composites in this case, exhibit low impact resistance since high stress is transferred from the polymeric matrix to the filler particles instantly. LS particles act as
stress concentration sites which restrict plastic deformation. Upon impact, the crack propagates to the interfacial regions and the material fails in a brittle manner. However, the impact properties of MAPE composites are observed to be much higher than pure HDPE due to the effective bonding at the filler-matrix boundary.

3.2. Tensile properties of lime sludge-coir-epoxy composites

Tensile properties were also studied for LS-epoxy and LS added with short coir fibre (8mm, 30 wt. %) in epoxy composites with LS varying from 0 to 12 wt. %. Specimen samples are shown in Fig. 1 (b). It is observed that for raw LS infused epoxy composites, the tensile strength continues to increase with up to 6 wt. % of lime sludge after which it starts decreasing. This indicates that LS acts as an effective reinforcement up to 6 wt. % in an epoxy matrix. A similar trend in the tensile properties is also observed for LS added coir-epoxy composites upon addition of LS. Herein, the highest strength is also observed at 6 wt. % LS. Subsequently, due to higher stress concentration (probable particle agglomeration) and interfacial dewetting, it starts decreasing thereafter. The tensile modulus continuously increases with increasing loading of rigid LS particles, thus resisting deformation within the elastic limit. In similar lines, the elongation at break drastically drops with increasing filler loading due to interfacial dewetting at the filler-matrix boundary and low ductility of rigid particulate fillers.

3.3. Thermal properties of lime sludge-coir-epoxy composites

Thermal parameters such as thermal degradation and % residual weight left at 500°C are used in order to study the effect of LS on the thermal properties of coir - epoxy composites. TGA curves are plotted for 3 and 9 wt. % LS added coir fibre - epoxy composites. The results calculated from the TGA thermograms are shown in Figure 2. In case of LS filled coir epoxy composites, the thermal degradation can be characterised by three stages. The first stage from 20°C to 240°C is due to the release of absorbed moisture in the fibres. The second stage (temperature range from 240°C to 425°C) is related to the degradation of cellulosic substances, such as hemicellulose and cellulose and also the degradation of epoxy matrix. The third stage (temperature range from 425°C to 500°C) of the decomposition is due to the degradation of non-cellulosic materials in the fibres. Since, lime sludge is mainly composed of CaCO₃; hence they are stable up to a temperature of 500°C. However, the higher residual weight % of 28% and 34% for both 3 and 9 wt. % LS filled coir-epoxy composites at 500°C is due to the presence of char after the decomposition of 30 wt. % coir fibres in the composite. Moreover, the extra 6 % of residual weight in case of 9 wt. % LS filled coir-epoxy composites is due to the higher content of stable LS present in the composite. This is also evident from the fact that at higher temperature the weight percentage loss of 3 wt. % LS composite was found to be larger than the 9 wt. % LS composite due to presence of higher non-decomposed LS in the latter case. This suggests that as the amount of lime sludge increases the composites become more thermally stable.

**Figure 2.** TGA thermograms of LS-coir-epoxy composites.

**Figure 3.** Water absorption property of LS-HDPE and LS-coir-Epoxy composites.
3.4. Water absorption (WA) properties of lime sludge-coir-epoxy composites

The WA behaviour of the LS filled HDPE and LS filled coir epoxy composites determined by Equation (1) is shown in Figure 3. Results suggest that the water absorption of the LS filled composites depend on parameters such as filler loading. Water absorption of the composites increases almost linearly in the initial stages and reaches a saturation limit beyond which there is no more water uptake by the composites. The water uptake increased with increasing filler loading from 10 to 30 wt. % suggesting more water uptake by the LS particles as higher filler loading. WA behaviour is also studied for composites with increasing coir fibre loading i.e. 10 and 35 wt. % coir fibre loading in the composite. Similar observations are also made in case of LS filled coir-epoxy composites i.e. the rate of water absorption increases with increase in fibre content. Composites with 35 wt. % fibre content shows more water absorption rate as compared to 10 wt. % fibre content. Cellulose coir fibres are hydrophilic in nature and cellulose fibres have a central hollow region (i.e. the lumen) which allows much water to be absorbed via the capillary effect. Thus, as fibre loading increases in the composites, more interfacial area exists leading to an increase in water absorption. Thus, due to the hydrophilic nature of cellulose fibres, composites reinforced with cellulose fibres always tend to absorb more water than other types of composites.

4.0. Conclusions

Industrial lime sludge waste is used as filler in HDPE, MAPE and coir-epoxy composites and it is found that LS is an attractive option as reinforcing filler in polymeric composites. Thus, improvement in the functionality and commercial viability of LS is evident in using LS waste as filler in polymeric composites resulting in low manufacturing cost. Results revealed that addition of lime sludge in polymeric matrix significantly increased the tensile and flexural modulus which can be attributed to increased stiffness due to the addition of rigid particulate fillers providing mechanical restraint to deformation. Mechanical properties (Tensile and flexural strength) of LS-MAPE composites are found to be superior to raw LS-HDPE composites and pure HDPE due to higher interfacial bonding at the filler-matrix boundary. The mechanical properties (tensile strength and modulus) also improved for LS filled coir-epoxy composites peaking at 6 wt. % LS proving that it to be an effective reinforcing agent in hybrid coir composites. Thermal stability of the composites increased with the addition of LS filler as is evident from the increase in residual weight % with increasing filler loading. Addition of LS and coir fibres increased the water absorption rate of the composites with increasing filler and fibre loading. LS as filler in HDPE composites and in coir-epoxy hybrid composites have proved itself to be an effective reinforcing agent. Thus, use of industrial lime sludge in polymeric composites would decrease the cost of composites in addition to decreasing the pollution caused by LS and producing composites with comparable properties.

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5.0. References

1. Joshi S V, Drzal L T, Mohanty A K and Arora S 2004 Composites A 35 371.
2. Saravana Bavan D and Mohan Kumar G C 2010 J. Reinf. Plast. Composites 29 3600.
3. Satyanarayana K G, Guimarães J L and Wypych F 2007 Composites A 38 1694.
4. Assessment of utilization of industrial solid wastes in cement manufacturing, Programme objective series. Technical report (PROBES/103/2006-2007), Central Pollution Control Board (Government of India), 2006.
5. Das O, Sarmah A K and Bhattacharyya D 2015 Waste Management 38 132.
6. Sommerhuber P F, Welling J and Krause A 2015 Waste Management 46 76.
7. Sommerhuber P F, Wang T and Krause A 2016 *J. Cleaner Production* **121** 176.
8. Guzel G and Huseyin D 2016 *Polymer Composites* doi:10.1002/pca.23962.
9. Chen J, Teng Z and Wu J 2015 *Polymer Composites* doi:10.1002/pca.23789.
10. Deepthi M, Sharma M, Sailaja R R N, Anantha P, Sampathkumaran P, Seetharamu S 2010 *Materials and Design* **31** 2051.
11. Liu L, Zhang Y, Lv F, Yang B and Meng X 2016 *Polymer Composites* **37** 2001.
12. Chen H, He H, Tian S, and Chen S 2016 *Polymer Composites* doi:10.1002/pca.24215.
13. Rout J, Misra M, Tripathy S S, Nayak S K and Mohanty A K 2001 *Composites Science and Technology* **61** 1303.
14. Geethamma V G, Mathew K T, Lakshminarayanan R. and Thomas S 1998. *Polymer* **39** 1483.
15. Ramprasath R and Jayabal, S 2016. *Polymer Composites* **37** 1765.
16. Rajamuneeswaran S and Jayabal, S. 2016 *Polymer Composites* **37** 844.
17. Matějka, V, Fu Z, Kukutschová J, Qi S, Jiang S, Zhang X, Yun R, Vaculík M, Heliová M and Lu Y, 2013 *Materials & Design*, **51** 847.