# Chapter 6

# Analysis of lime sludge filled various hybrid composites

An industrial waste which has to be used as a filler or reinforcement in polymeric composites needs to be versatile in its applications. Needless to say, it is a mandatory requirement for lime sludge waste to be resourceful enough to be used in polymeric matrices other than HDPE and with other reinforcing agents in hybrid composites. In this chapter, industrial lime sludge waste is used as filler in various hybrid composites *viz.* HDPE-MAPE blends, HDPE-PP blends, coir-HDPE-MAPE, epoxy, and coir-epoxy. This would throw some light on the versatility and feasibility of lime sludge waste as a reinforcing filler and its effects on the properties of composites when used with various polymeric matrices. In case of mechanical testing, five tests specimens were tested for each composite sample as per ASTM standards as mentioned in Chapter 3. The test results along with their means and standard deviation are tabulated in Appendix I. The graphical representation corresponding to the experimental results have been shown in this chapter for clarity.

## 6.1 Lime sludge filled HDPE-MAPE composites

The outright hindrance in using virgin particulate fillers in polymeric composites is low compatibility at the filler-matrix interfacial boundary. This is due to the hydrophilic nature of the polar fillers and hydrophobic nature of the non-polar polymeric matrices [128, 269]. Hence, inorganic fillers are immiscible in thermoplastic polymers such as polyolefins (HDPE, PP, LDPE etc.) and do not disperse easily. Due to strong intermolecular bonding, inorganic fillers tend to agglomerate during blending/mixing with a thermoplastic polymer as observed during the case of raw lime sludge filled HDPE composites (refer Section 4.3). Thus, a deterioration in mechanical and thermal properties of composites are observed due to this filler-matrix incompatibility and low interfacial adhesion at the filler-matrix boundary [6, 23, 265]. Hence, in the last few years, various methods have been proposed in order to improve the interfacial adhesion and compatibility at the filler-matrix interface so as to improve the properties of the composites. These methods include use of compatibilizers *viz.* maleic anhydride-grafting on polyolefins (such as HDPE and PP) [128, 269], the addition of coupling agents such as silanes, titanates etc [159], grafting the matrix with a hydrophilic functional group [265], chemical modification of filler surface [6, 23, 256] etc. The use of maleic anhydride grafted polymer (such as maleic anhydride gratef polyethylene (MAPE)) is very effective as a compatibilizing agent at the filler-matrix interface and has been used commonly in polymeric composites in order to improve their properties by enhancing the filler-matrix adhesion at the interface [128]. In the present study, lime sludge waste is used as a filler in HDPE-MAPE blends in varying weight fractions in order to study the effects of lime sludge and maleic anhydride compatibilizer on the composite properties.

### 6.1.1 Mechanical properties

Tensile, flexure, and Izod impact tests are conducted for lime sludge filled HDPE composites with a MAPE variation in each set of composites respectively. Herein, three sets of HDPE composites are tested with MAPE content varying as 1, 3, and 5 wt % and lime sludge content varying as 10, 20, and 30 wt % for each MAPE content respectively. This is in order to study the effect of MAPE compatibilizer on lime sludge filled HDPE composites in conjunction with raw and stearic acid coated lime sludge filled HDPE composites. Hence, comparative plots of the mechanical properties of raw, stearic acid coated and MAPE compatibilized lime sludge filled HDPE composites are shown in Figs. **??**(a-e). It may be noted that for comparative analysis with raw and stearic acid coated lime sludge filled HDPE composites, properties of 1 wt % MAPE compatibilized HDPE composites are compared with that of raw and coated lime sludge filled HDPE composites. The designation of composites depicting the respective weight fractions of the constituents (lime sludge, HDPE and MAPE) is shown in Table 6.1.

It is imperative to mention that the whole motivation behind using an industrial waste as filler in polymeric composites is low cost of the composites and reusing a material that causes environmental pollution. Since, MAPE is a costly material when compared with pure HDPE, hence, the ultimate goal is to use MAPE in smaller quantities which would increase the properties of the composites without affecting the commercial viability of the product. Hence, the properties of lime sludge filled HDPE-MAPE composites (MAPE is used as a compatibilizer) are discussed in this section.

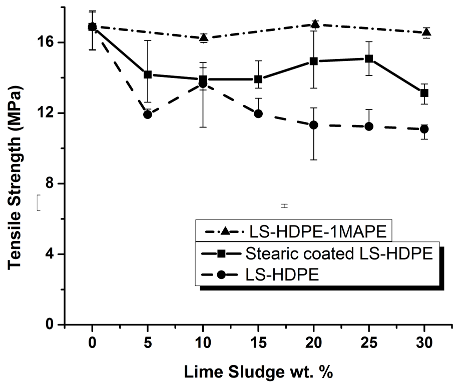
The test results of the composites are measured and tabulated in Table 6.1.

**Table 6.1:** Mechanical properties of lime sludge filled MAPE and HDPE-MAPE composites

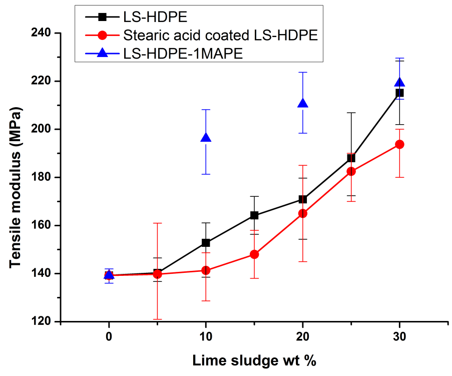
| Designation | Tensile strength (MPa) | Tensile modulus (MPa) | Elongation at break (%) | Flexural strength (MPa) | Flexural modulus (MPa) | Impact strength (J/m) |
|---|---|---|---|---|---|---|
| HDPE/LS/ MAPE (89/10/1) | 16.24±0.19 | 196.2±11.6 | 252±19.6 | 13.64±0.25 | 512±9.6 | 31.79±2.3 |
| HDPE/LS/ MAPE (79/20/1) | 16.99±0.15 | 210.5±9.9 | 40±11.0 | 14.47±0.20 | 595±11.1 | 40.26±1.4 |
| HDPE/LS/ MAPE (69/30/1) | 16.54±0.24 | 219.2±8.8 | 28±5.2 | 14.83±0.11 | 646±12.5 | 41.24±0.4 |
| HDPE/LS/ MAPE (87/10/3) | 16.58±0.25 | 198.5±8.5 | 210±11.8 | 14.09±0.18 | 521±13.7 | 39.14±0.7 |
| HDPE/LS/ MAPE (77/20/3) | 17.71±0.16 | 221.3±9.1 | 29±5.5 | 14.85±0.16 | 612±13.0 | 42.18±0.6 |
| HDPE/LS/ MAPE (67/30/3) | 16.91±0.30 | 260.3±12.2 | 27±4.7 | 15.89±0.19 | 683±7.1 | 44.36±0.4 |
| HDPE/LS/ MAPE (85/10/5) | 17.92±0.22 | 232.2±13.5 | 151±11.4 | 15.01±0.14 | 598±12.3 | 43.79±0.5 |
| HDPE/LS/ MAPE (75/20/5) | 18.59±0.26 | 256.8±11.4 | 23±4.8 | 15.14±0.09 | 652±13.0 | 44.34±0.2 |
| HDPE/LS/ MAPE (65/30/5) | 18.04±0.16 | 275.5±13.3 | 21±5.1 | 16.24±0.14 | 693±4.9 | 46.84±0.4 |

#### 6.1.1.1 Tensile properties

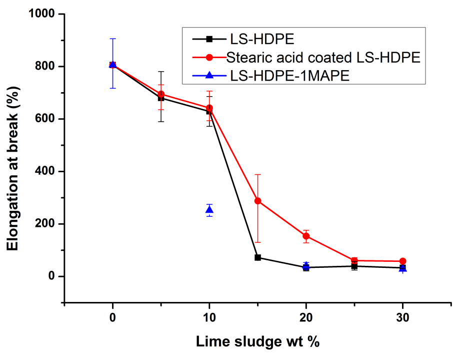
It is observed that the tensile strengths of lime sludge-MAPE composites are higher than that of raw and stearic acid coated lime sludge composites for all filler wt % (refer Sections 4.2.1 and 5.2 for properties of raw and coated lime sludge filled HDPE composites). Sample stress-strain curves for lime sludge filled HDPE with varying contents of MAPE as compatibilizer is shown in Figs. 6.2(a-c) and tensile properties are tabulated in Table 6.1. Higher tensile strengths of lime sludge-HDPE-MAPE composites indicate better physical interaction at the filler-matrix interface due to



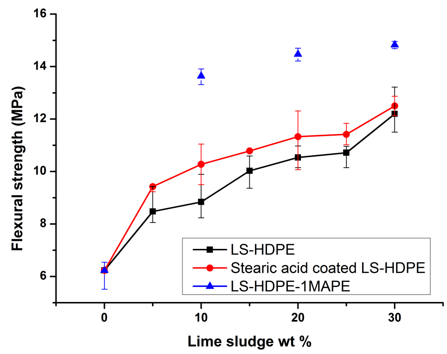

(a) Tensile strength.



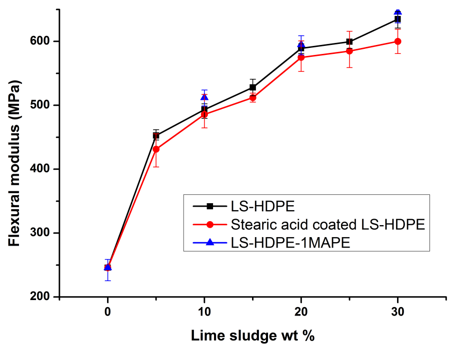

(b) Tensile modulus.



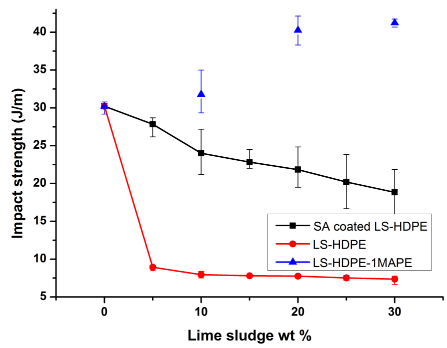

(c) Elongation at break.




(d) Flexural strength.




(e) Flexural modulus.




(f) Impact strength.

**Figure 6.1:** Comparative plots of the mechanical properties for uncoated, stearic acid coated and MAPE added lime sludge-HDPE composites.

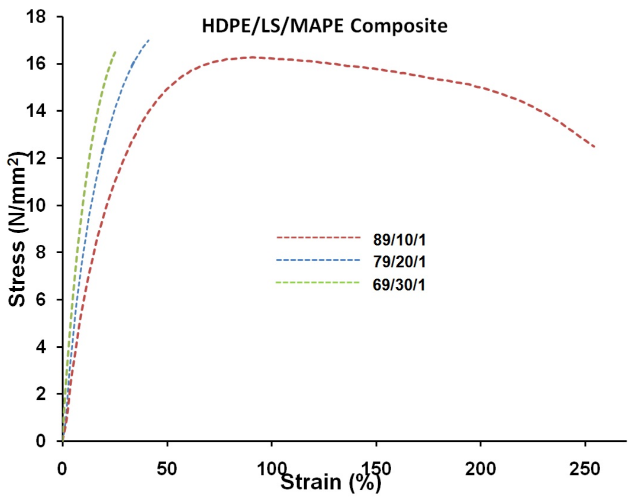
the presence of maleic anhydride compatibilizer grafted on the HDPE chains and resistance exerted by lime sludge particles to the propagation of the cracks. Lime sludge particles are hydrophilic in nature while the HDPE chains are hydrophobic, which causes weak interfacial bonding between the filler and matrix. Maleic anhydride grafting modifies the interface, thus providing stronger interfacial bonding (adhesion) at the filler-matrix interface along with proper dispersion of the filler in the matrix. This results in the increase in the tensile strength. However, at higher concentrations of above 20 wt % lime sludge, the tensile strength decreases due to filler particle agglomeration which creates stress concentration sites; thus, leading to crack initiation at these locations upon loading. Similar behaviour in the tensile properties shown by $CaCO_3$ based filler (kaolin) in a polymer matrix modified by maleic anhydride was also reported earlier by Salmah et al. [221].

A significant increment in the elastic modulus of lime sludge-HDPE-MAPE composites with increasing filler content is observed when compared with raw and stearic acid coated lime sludge composites due to (1) replacement of a polymeric matrix with rigid particles, thus restricting the chain mobility hindering deformation within the elastic limit; and (2) effective interfacial bonding between the filler and matrix resulting in efficient stress transfer within the elastic limit.

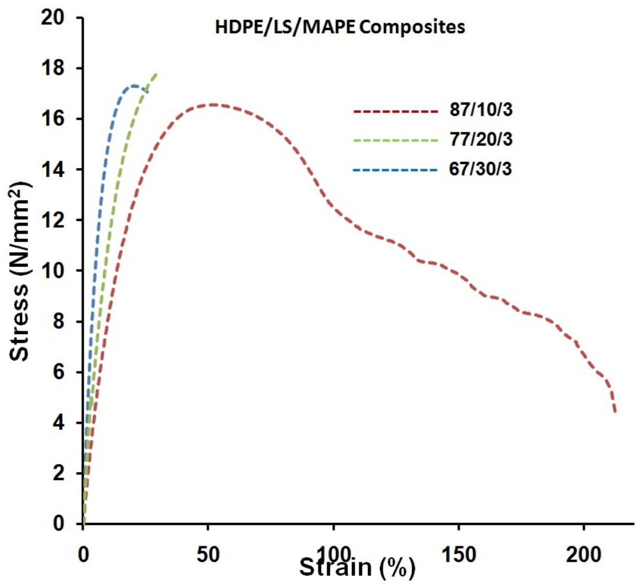
Elongation at break decreased significantly with increasing filler content which is a characteristic of particulate reinforced composites. Modification with maleic anhydride as compatibilizer has increased the tensile strength of composites with an enhancement in rigidity and reduction in the ductility of composites; this consequently lowered the elongation at break of the composites [221].

Thus, modification with MAPE as the compatibilizer has increased the tensile strength of composites, with an enhancement in the rigidity but reduced the ductility of composites.

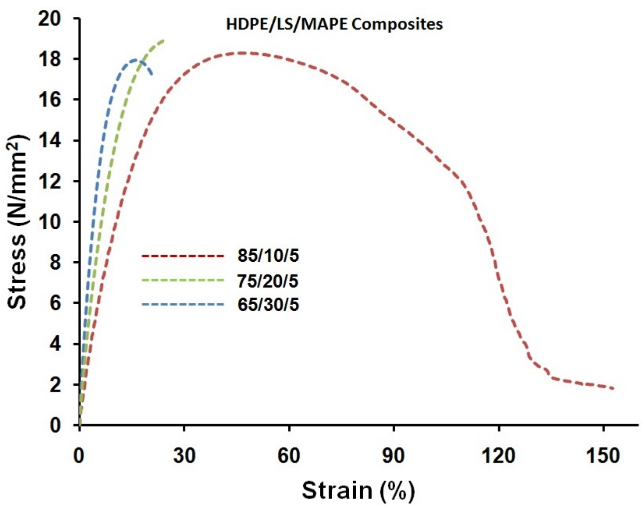
The evidence of improvement in the properties of the MAPE added lime sludge filled HDPE composites are further reinforced by the Fig. 6.4. It is observed in Fig. 6.4(a) that without the presence of a compatibilizer, the fractured surface revealed loose lime sludge particles which dissociate from the polymeric matrix upon loading due to low interfacial bonding; thus resulting in poorer mechanical properties. However, in case of MAPE added composites (refer Fig. 6.4(b)), it is observed that at the fractured surface, the lime sludge particles remain embedded in the matrix indicating effective bonding at the filler-matrix interface. Hence, it is morphologically evident that improved bonding ensures enhancement of mechanical properties of the MAPE added composites.




(a) 1 wt % MAPE.

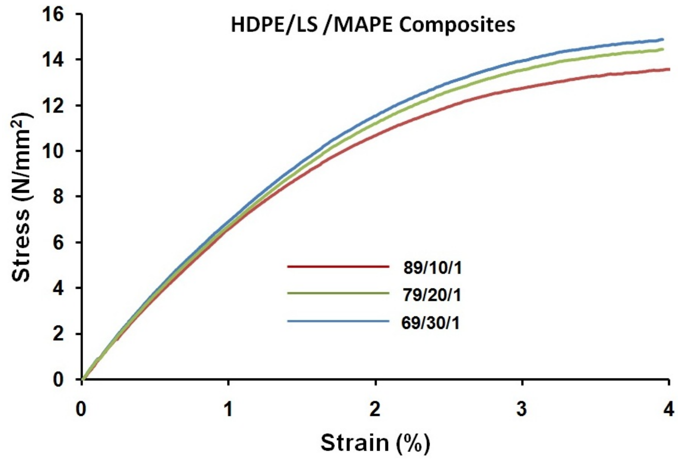



(b) 3 wt % MAPE.

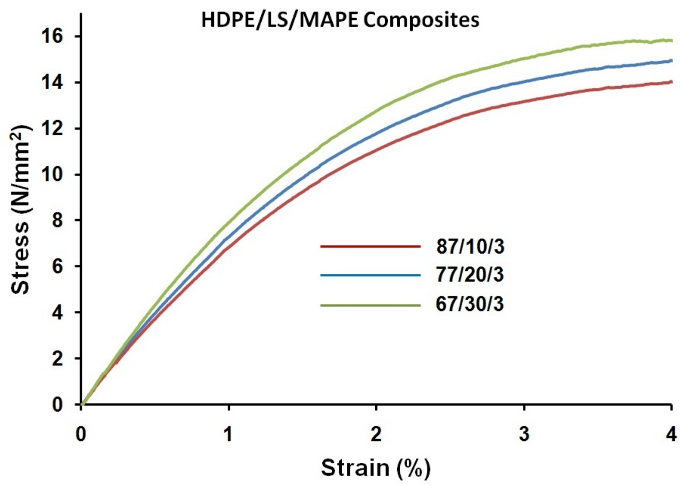



(c) 5 wt % MAPE.

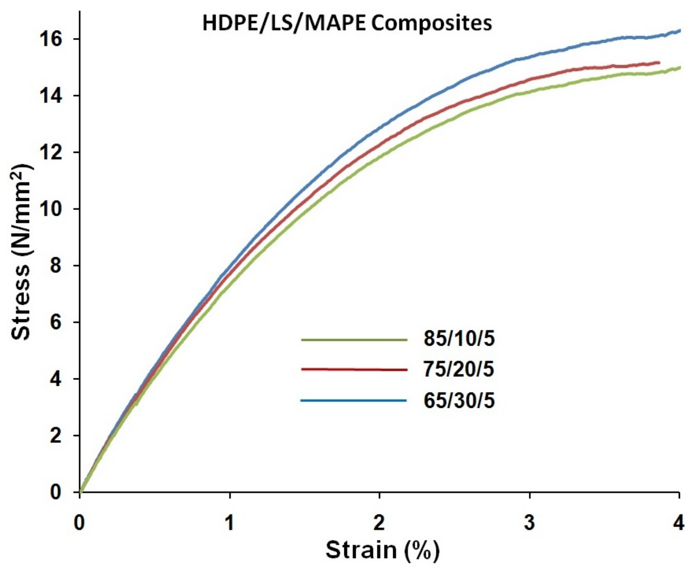
**Figure 6.2:** Sample stress-strain curves for lime sludge filled HDPE composites with MAPE as the compatibilizer derived after tensile testing.




(a) 1 wt % MAPE.

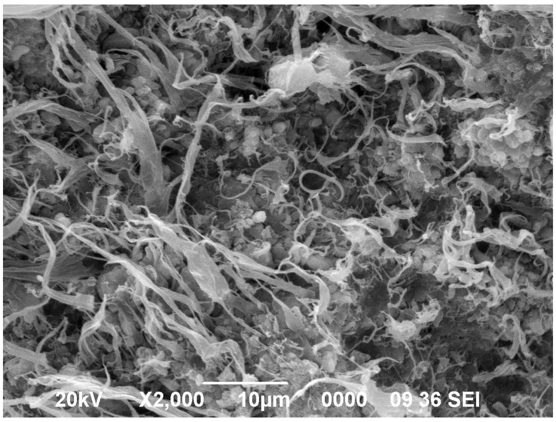



(b) 3 wt % MAPE.

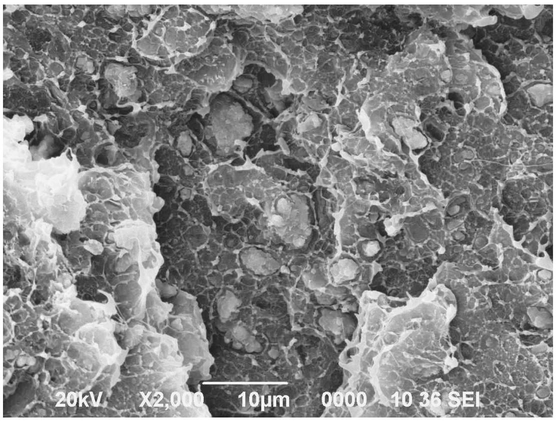



(c) 5 wt % MAPE.

**Figure 6.3:** Sample stress-strain curves for lime sludge filled HDPE composites with MAPE as the compatibilizer derived after flexural testing.




(a) HDPE/LS(70/30)




(b) HDPE/LS/MAPE(65/30/5)

**Figure 6.4:** SEM micrographs at the fractured surface of lime sludge filled HDPE and MAPE added lime sludge filled HDPE.

#### 6.1.1.2 Flexural and impact properties

Sample stress-strain curves under flexural conditions for lime sludge filled HDPE composites with varying contents of MAPE as compatibilizer is shown in Figs. 6.3(a-c) and the flexural properties are tabulated in Table 6.1. 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 lime sludge particles, HDPE and the maleic anhydride (MA) modified HDPE chains under bending stresses lead to better flexural strengths for HDPE-MAPE composites. Higher concentration of rigid particulate materials require higher stress for the same amount of deformation and hence, increase in the flexural modulus is also observed all the MAPE added composites.

It is observed that the impact strength of the lime sludge-HDPE-MAPE composites increased with increasing filler loading. MAPE improved the interfacial compatibility of lime sludge with the matrix as a result of which it could deliver more impact energy upon fracture. MAPE assumed the function of a bridge among the filler and HDPE matrix; and thus, improved the interfacial condition in each component. Hence, the impact strength of composites improved much more than that observed for raw and stearic acid coated lime sludge-HDPE composites. Similar observations in the increase in the flexural and impact properties was reported earlier by Zhou et al. [284] where MAPE was used as the compatibilizer in carbon fibre/wood plastic composites.

It is interesting to note that out of all the three MAPE contents used ( *i.e.* 1, 3 and 5 wt %), a MAPE content of 5 wt % proved to be the optimum weight fraction of MAPE in the composites which would result in the best mechanical properties among all the three sets of composites. This suggests that a weight fraction of 5 wt % MAPE provides the most effective interfacial adhesion at the filler-matrix boundary, thereby improving the mechanical properties.

## 6.2 Lime sludge filled HDPE-PP blends

Properties of conventionally used structural materials made from polymeric composites has been pushed to their limits in recent times, hence, the opportunity to develop products with superior properties through polymer blend based composites have generated vigorous interest among researchers [72]. It is expected that substitution of pure polymer-based composites with polymer blend-based composites would generate composites with a better property to cost ratio. In addition to using pure polymer, polymer blends are in vogue nowadays, as they are cheap and provides scope for development of composites with unique properties. Polypropylene/polyethylene blends are widely studied polymer blends [173, 175, 279, 280]. Various polyethylene grades *viz.* low-density polyethylene (LDPE), high-density polyethylene (HDPE), and linear low-density polyethylene (LLDPE) were earlier used to modify the physical and mechanical behaviour of polypropylene (PP) by blending the polymers together in different weight fractions [57]. Blending of polymers is an economical and convenient means of customizing a polymeric material as per a specific requirement which cannot be satisfied by a single virgin polymer. Hence, blending of the polymers is commonly done to control the microstructure and physical properties of these blends which would diversify their areas of applications.

Blending is done to incorporate the attractive properties of both the polymers while suppressing their limitations. In the present scenario, blending of polypropylene (PP) is done with various weight fractions of HDPE. Advantages of using PP is its high strength, stiffness and thermal stability; but it has poor impact resistance. On the contrary, HDPE has high impact resistance and relatively average stiffness, strength and thermal resistance [65]. Hence, HDPE-PP blends would be an attractive compromise with better impact resistance, strength, stiffness and thermal stability than pure HDPE. Additionally, HDPE-PP blends are also cheaper than ethylene-propylene copolymer as their preparation involves mixing of the two molten polymers in an extruder, as opposed to controlled and specialized polymerization process required by copolymers [65].

In a bid to study the effects and feasibility of lime sludge waste being used as a filler in polymeric blends, various HDPE-PP blend based composites are prepared with varying weight fractions lime sludge. This would throw some light on the behaviour of lime sludge waste as a filler material in polymeric blends; whether or not the effects of lime sludge addition is similar in single polymers and polymeric blends. The mechanical (tensile properties and hardness) and thermal properties of the lime sludge filled HDPE-PP blends are studied in the following sections.

### 6.2.1 Mechanical properties

Tensile test is carried out for lime sludge filled HDPE-PP blends samples in order to study the effect of lime sludge addition on the mechanical properties of the newly formed composites. Mechanical properties such as tensile strength, elongation and Shore D hardness of the composites are measured and the results are tabulated in Table 6.2. Sample stress-strain curves for lime sludge filled HDPE-PP blends is shown in Fig. 6.5.

**Table 6.2:** Mechanical properties of lime sludge filled HDPE-PP composites.

| Designation | Tensile strength (MPa) | Tensile modulus (MPa) | Elongation at break (%) | Shore D hardness |
|---|---|---|---|---|
| Pure PP | 31.47 ± 0.24 | 392 ± 11.0 | 19.2 ± 2.8 | 70 ± 0.6 |
| 5LS-85H-10P | 7.58 ± 0.19 | 164 ± 11.5 | 165.0 ± 13.4 | 63 ± 1.8 |
| 10LS-80H-10P | 9.57 ± 0.16 | 195 ± 12.5 | 148.2 ± 10.5 | 65.5 ± 1.4 |
| 15LS-15H-70P | 9.84 ± 0.12 | 276 ± 12.1 | 10.2 ± 1.9 | 66 ± 0.70 |
| 20LS-10H-70P | 12.75 ± 0.20 | 292 ± 7.8 | 10 ± 2 | 71 ± 0.62 |

#### 6.2.1.1 Tensile strength

The tensile strength of HDPE and PP are approximately 16.88 MPa (refer Fig. 4.6(a)) and 31.46 MPa respectively. It is observed that the tensile strength of all the composite samples are less than the tensile strength usually observed in pure forms of both HDPE and PP. The deterioration of tensile strength in the lime sludge filled composites when compared with that of pure HDPE and PP may be attributed to dewetting at the filler-matrix boundary on account of poor bonding. The blends are not compatible due to poor interfacial adhesion between the reinforcing components and the polymers. Hence stress transfer does not take place between the components [114]. Additionally, higher stress concentration sites created by the lime sludge particles lead to void formation due to pull out of particles upon stretching. Moreover, $CaCO_3$ (present in lime sludge) is known to promote crazing during deformation of polymers leading to fracture [141]. However, it is also observed that at a constant PP wt % of 10, the tensile strength increases from 7.58 to 9.57 MPa upon increasing the filler loading from 5 to 10 wt % (which also results in decrease in HDPE wt % from 85 to 80). Similarly, at a constant PP wt % of 70, the tensile strength increases from 9.84 to 12.75 MPa upon increasing the filler loading from 15 to 20 wt %. This suggests effective lime sludge reinforcement up to 20 wt % in HDPE-PP blends. The increment in tensile strength may also be attributed to the increment in the wt % of PP from 10 to 70 wt %. Since, properties of polymer blends are weighted averages of its constituents, PP with higher tensile strength values than HDPE also contributes to the increase in the tensile strength. However, the effect of lime sludge in reinforcing HDPE-PP blends is significant in this case when the jump in the tensile strength values from 7.58 to 9.57 MPa (for 5 to 10 wt % lime sludge) and from 9.84 to 12.75 MPa (for 15 to 20 wt % lime sludge) at constant PP weight fractions of 10 and 70 wt % respectively.

#### 6.2.1.2 Tensile modulus

The tensile modulus increased significantly with the addition of rigid lime sludge particles and introduction of a mechanical restraint due to the restriction in deformation provided by the addition of particulate filler. However, an interesting aspect of polymer blends when compared with single polymeric matrix is observed in this case. Although the tensile modulus increases continually with increasing filler loading, a sudden jump from 195 $\pm$ 18 to 276 $\pm$ 14 MPa was noticed when the PP wt % increased from 10 to 70 wt %. This is due to the fact that since the tensile modulus of virgin PP (i.e. 392 $\pm$ 32 MPa) is found to be much higher that HDPE-PP blends, addition of increasing wt % of PP in the composite contributes to the increment in the tensile modulus. Thus, it may be stated that the tensile modulus increased due to the addition of rigid lime sludge particles as well as with the increment in PP wt % in the composites. The results obtained in this case follows a similar trend to that obtained in earlier researches on polymeric blends and composites [90, 114].

#### 6.2.1.3 Elongation at break

The elongation at break decreased with increasing lime sludge filler content which is a typical trait of any particulate thermoplastic composite. Low elongation property of lime sludge filler restricts the flow of polymer molecules past each other. Moreover, the primary factors affecting the low elongation property of lime sludge filled HDPE-PP blends are - (1) rigidity of filler particles and (2) deformation at high stress concentration points around particles [20]. Additionally, the elongation at break (%) of the composites is higher when PP wt % is lower (10 wt %) while it decreased at the PP content increased to 70 wt % indicating that the increase in the PP content affected the ductility of composites adversely as the inherent ductility of PP is very low (elongation at break = 19 ± 3 %). Since, the elongation at break (%) for HDPE is in excess of 800 % (refer Fig. 4.7), hence, the ductility of the composites where HDPE content is high, show much higher ductility i.e. for 80 and 85 wt% HDPE, elongation values are 165 ± 4 % and 148 ± 6 respectively.

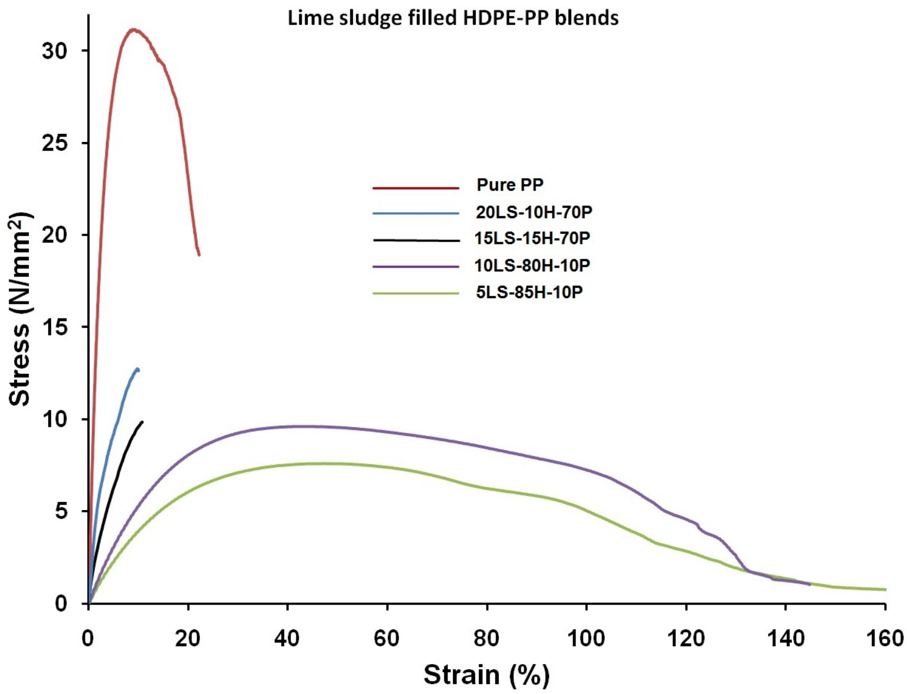



**Figure 6.5:** Sample stress-strain curves for PP and lime sludge filled HDPE-PP blends derived after tensile testing.

#### 6.2.1.4 Shore D hardness

It is observed that the shore D hardness of HDPE and PP are 61.5 ± 0.5 and 70 ± 1 respectively (refer Tables 6.3 and 6.2). As shown in in Table 6.2, it is observed that in case of lime sludge filled HDPE-PP blends, the shore D hardness increased with increasing weight fraction of lime sludge and PP in the composite. This may be due to two reasons - (1) addition of rigid lime sludge particles in a soft matrix which leads to increase in the hardness due to the increase in the rigidity and stiffness of the brittle composites, and (2) since the hardness value of pure PP is on the higher side (70 ± 1), hence addition of more PP n the blend increased the hardness values. However, it is also important to note that hardness is a surface property. Additionally, it is also reported in earlier studies that the hardness values of HDPE-PP blends obtained were above the additive line [114]. Since, the hardness values of lime sludge filled HDPE-PP blends did not clearly deduce the effect of lime sludge on the hardness values, hence, in order to determine the actual effect of lime sludge on the hardness of the composites, shore D hardness values are determined for lime sludge filled HDPE composites (5, 10, 15, 20, 25 and 30 wt % lime sludge in HDPE matrix) as shown in Table 6.3. It is observed that the hardness of composites increased with increasing weight fraction of lime sludge in the polymeric matrix. Hence, it is evident that lime sludge is instrumental in increasing the hardness of the composites by increasing the rigidity and stiffness of the composites due to the addition of rigid lime sludge particles in a softer matrix.

**Table 6.3:** Shore D hardness of lime sludge filled HDPE composites.

| Designation | Shore D hardness |
|---|---|
| Pure HDPE | 61.5 ± 0.8 |
| 5 LS HDPE | 62 ± 0.5 |
| 10 LS HDPE | 64 ± 0.8 |
| 15 LS HDPE | 66.5 ± 0.35 |
| 20 LS HDPE | 67.5 ± 0.8 |
| 25 LS HDPE | 68 ± 0.8 |
| 30 LS HDPE | 69 ± 0.8 |

## 6.2.2 Thermal properties

The effect of lime sludge addition on the thermal properties of HDPE-PP blends is discussed in this section. The thermal properties were characterized using DSC and TG techniques. Lime sludge filled HDPE-PP blends with varying constituent contents are analyzed and compared with pure HDPE and PP. Samples are chosen so that there is an increment in the lime sludge content by 5 wt % (from 15 to 20 wt %) at a constant PP content of 70 wt % in order to study the effect of lime sludge on the thermal properties of the composites.

### 6.2.2.1 DSC analysis

DSC analysis is carried out in order to determine the thermal parameters such as melting temperature ($T_m$), crystallization temperature ($T_c$), onset melting temperature ($T_{on}$), heat of fusion ($H_f$) and degree of crystallinity ($\chi_c$). The values of the thermal parameters are recorded from the DSC heating and cooling thermograms as shown in Figs. 6.6(a) and 6.6(b) respectively and are tabulated in Table 6.4. Samples 15LS-15H-70P and 20LS-10H-70P with varying lime sludge weight fraction of 15 and 20 wt% are characterized using DSC techniques and compared with pure HDPE in order to understand the effect of lime addition on the various factors mentioned above.

The degree of crystallinity of pure HDPE is calculated using Eq. (4.1). Thus, the degree of crystallinity of HDPE and PP components in the composites are calculated using Eq. (6.1)and (6.2) respectively. The heat of fusion for 100 % crystalline HDPE ($H^{o}_{mHDPE}$) and PP ($H^{o}_{mPP}$) are taken as 293 J/g and 209 J/g respectively [279].

$$\chi_{cHDPE} = \frac{H_{mHDPE}}{H^{o}_{mHDPE} w_{HDPE}} \times 100 \tag{6.1}$$

$$\chi_{cPP} = \frac{H_{mPP}}{H^{o}_{mPP} w_{PP}} \times 100 \tag{6.2}$$

The DSC thermogram (refer Figs. 6.6(a)) shows that HDPE-PP blends possess

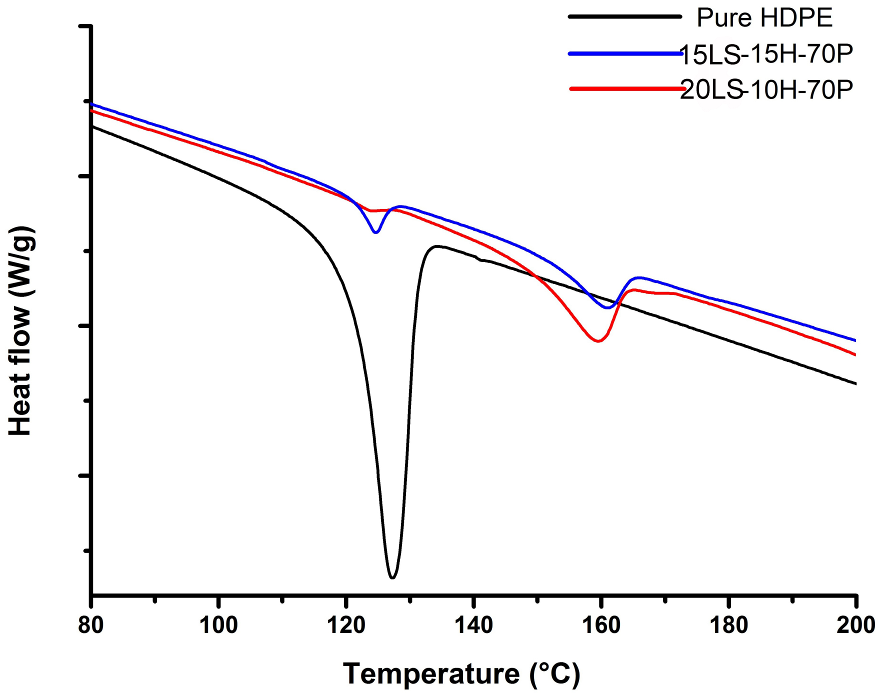
**Table 6.4:** DSC analysis of lime sludge filled HDPE-PP composites.

| Sample | $T_{on}$(°C) | | $T_m$(°C) | | $T_c$(°C) | $H_f$(J/g) | | $\chi_c$(%) | |
|---|---|---|---|---|---|---|---|---|---|
| | HDPE | PP | HDPE | PP | | HDPE | PP | HDPE | PP |
| Pure HDPE | 121.7 | - | 126.83 | - | 112.10 | 228 | - | 77.66 | - |
| 15L-15H-70P | 121.7 | 154.29 | 125.41 | 161.57 | 112.04 | 20.4 | 39.54 | 46.32 | 27.03 |
| 20L-10H-70P | 121.17 | 153.16 | 124.55 | 160.62 | 108.05 | 5.57 | 66.24 | 12.63 | 40.06 |

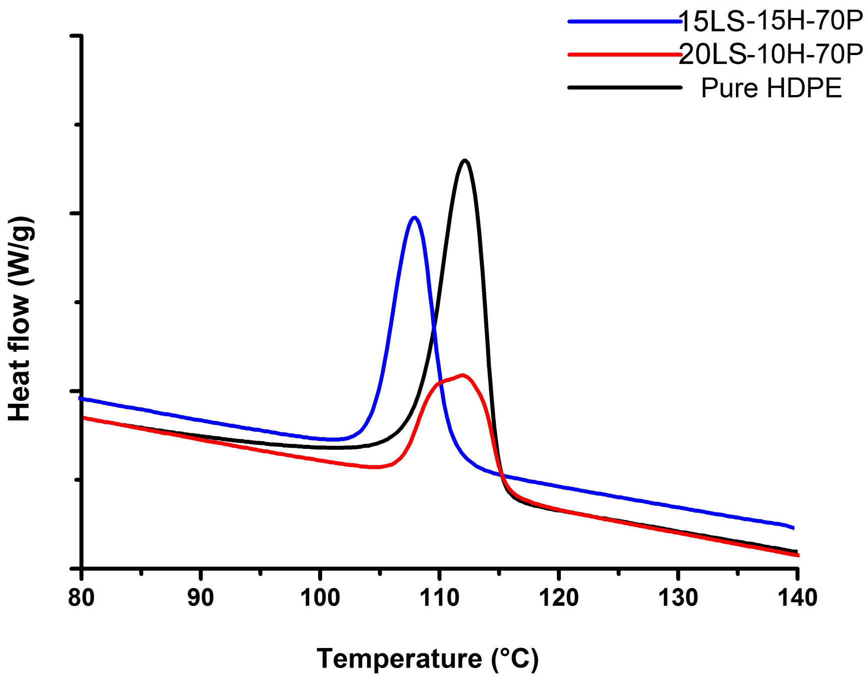
two melting peaks, indicating that PP and HDPE co-exist in the composite. It is observed that the effect of adding lime sludge in HDPE-PP blends is insignificant in terms of onset melting and melting temperatures of both HDPE and PP as the changes in temperatures are very small.

It is observed that the melting enthalpy decreased for HDPE (from 20.4 to 5.57 J/g) as its wt % decreased by 5 and lime sludge increased by 5 wt %. On the contrary, the melting enthalpy of PP increased (from 39.54 to 66.24 J/g). However, the overall total additive melting heat enthalpy of the HDPE-PP blend decreased with the addition of lime sludge upon blending than that in case of pure HDPE (293 J/g) and PP (209 J/g) respectively. This behaviour is similar to that of lime sludge filled pure HDPE composites. This indicates that the required heat to melt the composite decreased which accounts for easier extrusion and molding conditions, thus saving money and power [71].

It is observed in literature that the degree of crystallinity of one component in a HDPE-PP blend decreases as the mass fraction of the other component increases in




(a) Heating cycle.




(b) Cooling cycle.

**Figure 6.6:** DSC thermogram during heating and cooling cycles for lime sludge-HDPE-PP blends and pure HDPE.

the blend to a certain extent [279]. The degree of crystallinity of HDPE increased drastically (12.63 % to 46.32 %) with the increase in the weight fraction of HDPE by only 5 %. Nevertheless, the increase in crystallinity can also be contributed by lime sludge particles acting as heterogeneous nucleation sites. Additionally, the drastic increase in crystallinity from 27.03 % to 40.06 % (for constant 70 wt % of PP) with HDPE decreasing by 5 wt % and lime sludge increasing by 5 wt %, can be attributed to the addition of lime sludge particles acting as heterogenous nucleation sites for the crystallites, thereby increasing the crystallinity. This phenomenon of particulate fillers acting as nucleating agents in polymeric composites have been reported in various other previous studies [55, 141, 194].

#### 6.2.2.2 TG analysis

Thermal stability of the composites 10LS-80H-10P and 15LS-15H-70P fabricated with varying lime sludge weight fraction of 10 and 15 wt% are characterized using DSC techniques and compared with pure HDPE and PP using TGA by measuring the onset degradation temperature ($T_m$) and % residual weight left at 600 °C. The TGA curves for the composite samples 10LS-80H-10P and 15LS-15H-70P along with pure HDPE and PP are plotted as shown in Fig. 6.7.

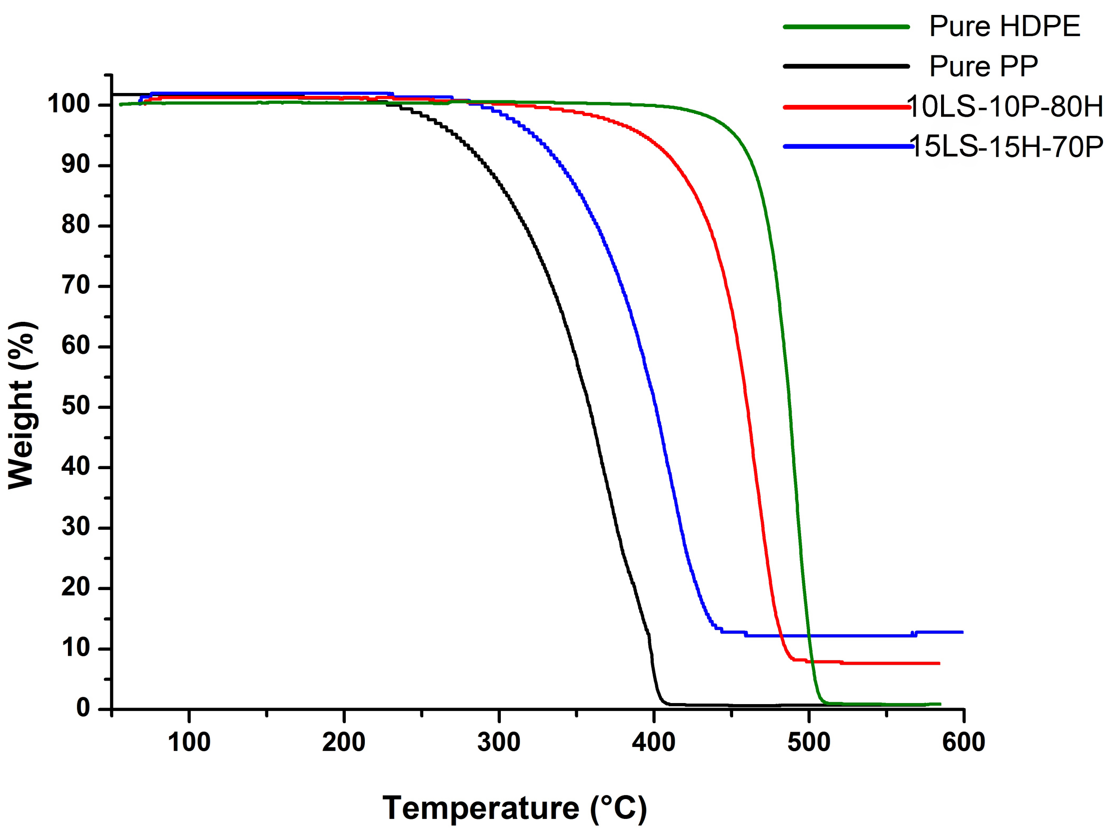



**Figure 6.7:** TGA thermograms of lime sludge filled HDPE-PP composites and pure polymers.

The values of thermal degradation parameters are measured from the TGA thermograms and tabulated in Table 6.5.

**Table 6.5:** TGA results of pure HDPE and lime sludge – HDPE composites

| Sample | Residual weight % | $T_{on}$ (°C) |
|---|---|---|
| Pure HDPE | 429.19 | 0.71 |
| 10L-80H-10P | 417.35 | 7.44 |
| 15L-15H-70P | 352.31 | 12.57 |
| Pure PP | 317.08 | 0.71 |

It is a commonly known fact that HDPE is more thermally stable than PP. Hence, the TGA plots and the onset degradation temperatures of the HDPE-PP blends filled with lime sludge are observed in between that of pure PP (on the lower side) and pure HDPE (on the higher side) respectively; a phenomenon observed for most polymeric blends since the properties of polymer blends are weighted averages of its constituents. Hence, it is observed that the onset degradation temperature of the composites increased with increasing weight fraction of HDPE in the lime sludge filled HDPE-PP blend (*i.e.* between the onset degradation temperatures of PP and HDPE respectively). This conforms well as HDPE degrades thermally at higher temperatures than PP. Additionally, it was also observed earlier in case of lime sludge filled pure HDPE composites (refer section 4.2.2.2) that lime sludge is also instrumental in increasing the thermal stability of the composites. Hence, the rise in the thermal stability of lime sludge filled HDPE-PP blends may also be attributed to the addition of lime sludge. This idea also reinforced by the fact that the residual weight % of the composites improved with rising lime sludge loading in the composites. It is observed that the residual weight % at 600 °C is higher for the lime sludge filled composite blends than that of pure HDPE and PP. Thus, it may also be stated that lime sludge addition increased the thermal stability of the HDPE-PP blends.

## 6.3 Lime sludge filled coir-HDPE-MAPE hybrid composites

In this study, randomly dispersed short coir fibres (8 mm long) and lime sludge were chosen as fillers in HDPE matrix. Additionally, MAPE is also used as a coupling agent in order to increase the interfacial adhesion at the filler-matrix boundary. Coir fibre (CF) is used because in addition to mitigating environmental issues of using hazardous and non-biodegradable synthetic materials, natural fibres also offer advantages such as low cost, versatility, lightweight, biodegradability, renewability, high specific strength and modulus, lower equipment abrasion, and low energy consumption during processing [235]. Coir fibre also has low cellulose content, high microfibrillar angle, not as brittle as glass fibre, can be chemically surface modified, is non-toxic (no waste disposal issues), water proof, resistant to salt water, and has lower tensile strength and high elongation compared to other lignocellulosic fibres [111, 165].

Thus, incorporation of lime sludge waste into fibre reinforced polymeric composites can propose some routes towards exploring new alternatives of developing a new hybrid composite, which would in turn increase its economic value. Hence, this study would throw some light on the effects of lime sludge on the mechanical properties of the coir-HDPE-MAPE hybrid composites.

The test results of the composites are measured and tabulated in Table 6.6. Sample stress-strain curves under tensile conditions for coir-HDPE, coir-HDPE-MAPE and lime sludge filled coir-HDPE-MAPE are shown in Figs. 6.9(a-c). Additionally, sample stress-strain curves under flexural conditions for coir-HDPE, coir-HDPE-MAPE and lime sludge filled coir-HDPE-MAPE are shown in Figs. 6.10(a-c). Initially, the effects of coir and MAPE on HDPE matrix are discussed in order to assess the effects of coir on the mechanical properties of the composites. This is done in order to first determine the effective coir content in the composite which would exhibit superior properties. The coir content which shows optimum properties is then selected for fabrication of lime sludge-coir-HDPE composites with varying lime sludge content. Since, 5 wt % MAPE earlier proved to be the optimum amount of compatibilizer in case of LS-HDPE-MAPE composites; hence, a weight fraction of 5 wt % MAPE compatibilizer is fixed for studying the properties of LS-coir-HDPE-MAPE composites.

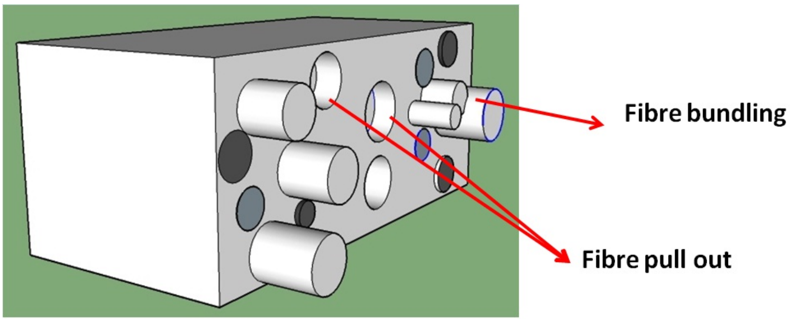
### 6.3.1 Effect of fibre loading on coir-HDPE composites

The properties of coir-HDPE composites with varying fibre content (10, 20 and 30 wt %) are shown in Table 6.6. It is observed that the tensile strength of coir-HDPE composites increased by 19.8 % when coir content increased from 10 wt % to 20 wt %. This initial increase may be attributed to the effective reinforcement offered by randomly distributed short coir fibres in the HDPE matrix. However, the tensile strength decreased upon addition of more coir fibres (at 30 wt %) due to dewetting at the fibre-matrix boundary and fibre bundling; thereby resulting in crack initiation at these locations upon loading. Similar trend in the tensile strength was reported

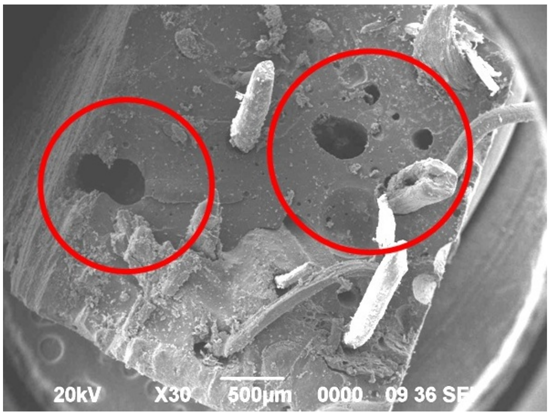
**Table 6.6:** Mechanical properties of lime sludge filled coir-HDPE-MAPE composites.

| Designation | Tensile strength (MPa) | Tensile modulus (MPa) | Elongation at break (%) | Flexural strength (MPa) | Flexural modulus (MPa) | Impact strength (J/m) |
|---|---|---|---|---|---|---|
| HDPE/CF (90/10) | 15.11±0.84 | 236.5±20.2 | 63.16±14.70 | 11.55±0.31 | 311.2±13.19 | 20.57±1.70 |
| HDPE/CF (80/20) | 18.85±0.58 | 258.2±21.6 | 22.68±6.25 | 12.27±0.31 | 375.3±15.72 | 18.06±1.11 |
| HDPE/CF (70/30) | 15.96±0.51 | 275.8±17.7 | 10.85±2.01 | 12.71±0.46 | 391.6±14.08 | 17.53±0.41 |
| HDPE/CF /MAPE (85/10/5) | 22.67±0.39 | 311.2±18.1 | 78.15±10.45 | 12.13±0.26 | 311.3±12.30 | 22.97±0.80 |
| HDPE/CF /MAPE (75/20/5) | 29.63±0.47 | 336.9±17.8 | 48.76±6.31 | 12.79±0.41 | 338.5±13.33 | 20.98±0.77 |
| HDPE/CF /MAPE (65/30/5) | 22.46±0.39 | 364.2±25.3 | 34.38±4.78 | 14.54±0.36 | 405.3±10.66 | 19.33±0.56 |
| HDPE/LS/ CF/MAPE (65/10/20/5) | 24.16±0.36 | 321.5±14.8 | 52.44±6.60 | 17.56±0.40 | 437.4±10.73 | 20.68±0.63 |
| HDPE/LS/ CF/MAPE (60/15/20/5) | 34.49±0.39 | 345.1±17.4 | 35.62±5.21 | 19.42±0.29 | 453.7±15.33 | 19.50±0.35 |
| HDPE/LS/ CF/MAPE (55/20/20/5) | 25.39±0.47 | 378.6±14.9 | 14.90±4.93 | 21.55±0.44 | 475.8±13.80 | 18.14±0.41 |

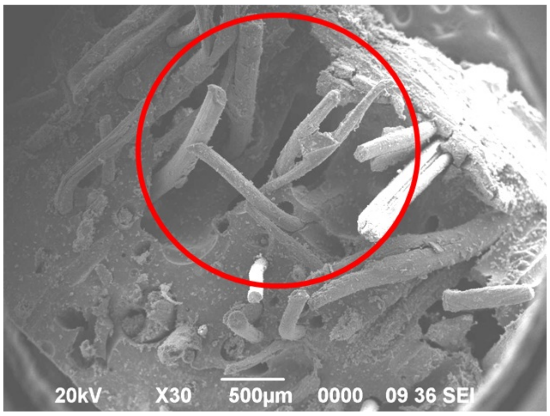
earlier during testing of bagasse fibre [140] and rice straw fibre [272] reinforced composites. However, stiffness and rigidity of the composites increased upon fibre loading as the tensile modulus increased by 14 % as coir fibre content increased from 10 wt % to 30 wt %. This increase in the stiffness upon addition of coir is due to the high stiffness of the fibres [22]. Needless to mention that with the increase in the stiffness and strength of the composites, the ductility of the composites is bound to decrease significantly as shown in Table 6.6. This significant decrease in the elongation at break of 82.8 % with increasing fibre content may be attributed to the destruction of structural integrity upon loading due to interfacial dewetting (fibre pull out), increasing stiffness and fibre bundling at higher fibre content [214]. Line diagram and SEM images depicting coir fibre pull out and fibre bundling at 30 wt % coir loading is shown in Fig. 6.8.




(a) fibre pull-out and fibre bundling.




(b) fibre pull-out.




(c) fibre bundling.

**Figure 6.8:** Coir fibre pull-out from matrix (interfacial dewetting) and fibre bundling in 30 wt % coir reinforced lime sludge filled HDPE composites.

The flexural properties improved with increasing fibre content in the coir-HDPE composites. However, the difference in the increase of flexural strength was not significant i.e. 11.55 MPa for 10 wt % to 12.71 MPa for 30 wt % of coir. The flexural modulus increased significantly from 311.2 MPa for 10 wt % to 391.6 MPa for 30 wt % coir fibre loading. A similar trend in the flexural behaviour was reported earlier by Bettini et al. [40] for PP-coir fibre composites. They attributed this increase in the flexural properties to the mobility of the amorphous region, which becomes increasingly restrained owing to the presence of fibres that are stiffer than the polymer matrix.

Addition of coir fibres resulted in the decrease in the Izod impact strength when compared with pure HDPE *i.e.* 30.33 J/m for pure HDPE to 17.53 J/m for 30 wt % coir fibre loading. This decrease in the impact strength was due to the presence of coir fibres in the polymeric composites, which reduced the energy absorbed upon impact loading, resulting in reduced impact toughness. Similar decrease in the impact strength of polymeric composites upon addition of natural fibres was also reported earlier by various researchers [140, 272] who attributed it to the poor interfacial adhesion at the fibre-matrix boundary.

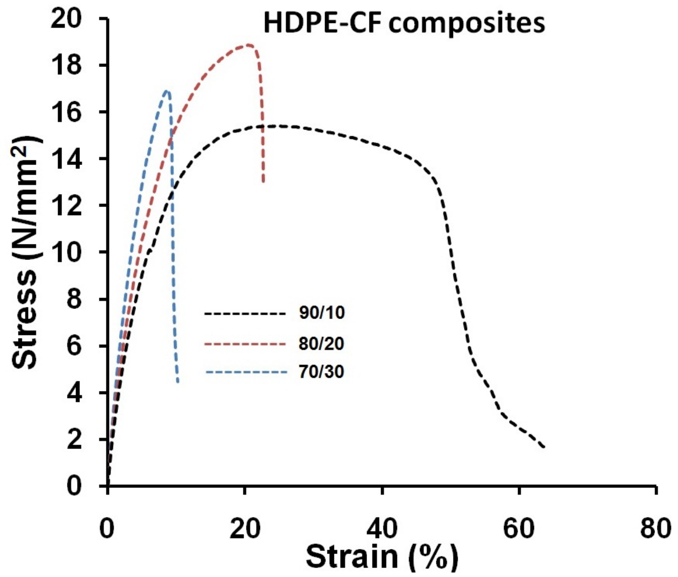
### 6.3.2 Effect of MAPE on coir-HDPE composites

The properties of coir-HDPE composites with 5 wt % of MAPE as compatibilizer and varying fibre content (10, 20 and 30 wt %) are shown in Table 6.6. Use of MAPE as a compatibilizer in coir-HDPE composites significantly improved almost all properties of the composites which is in agreement with the results reported earlier by other researchers [52, 140]. Although similar trends in the increase or decrease in the mechanical properties are shown by MAPE compatibilized composites when compared to neat coir-HDPE composites, the values obtained are far superior for MAPE compatibilized composites. This increase in the mechanical properties with the addition of 5 wt % MAPE compatibilizer may be attributed to the reaction between the hydroxyl groups of the coir fibres and the anhydride groups of the compatibilizer resulting in the formation of an ester linkage at the interface [45]. Additionally, the flexible polyethylene chains of MAPE can diffuse into the HDPE matrix and coir fibre bundles, improving the continuity of the system. This would decrease the void content between the fibres and matrix, thereby increasing the interfacial adhesion at the filler-matrix boundary resulting in the increase in the mechanical properties [172, 228].

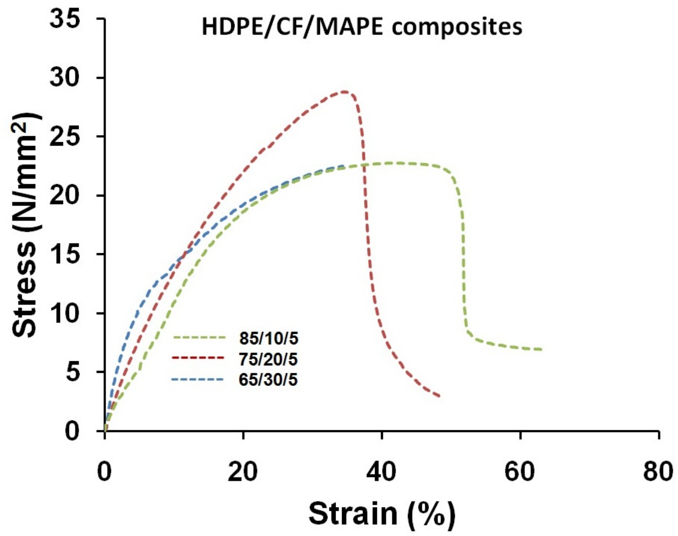
### 6.3.3 Effect of lime sludge on coir-HDPE-MAPE composites

Since coir-HDPE composites showed optimum properties at 20 wt % fibre content, this fibre content is chosen for fabrication of lime sludge filled coir-HDPE-MAPE composites with varying weight fraction of lime sludge (10, 15 and 20 wt%) in them. 5 wt % of MAPE is used as the compatibilizer as it earlier proved to be the optimum wt % in case of LS-HDPE-MAPE composites.

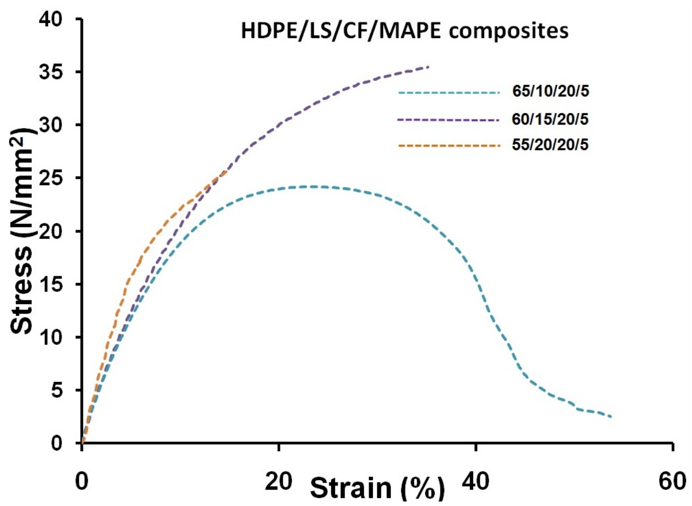
The properties of the composites are tabulated in Table 6.6. It is observed that the tensile strength increased from 24.16 MPa to 34.48 MPa when the lime sludge loading increased from 10 to 15 wt %, owing to effective reinforcement and dispersion of lime sludge particles in the matrix [230]. Upon further increment in the filler loading to 20 wt %, the tensile strength decreased to 25.39 MPa indicating agglomeration of lime sludge particles resulting in higher stress concentration sites and filler-filler interaction being more dominant than filler-matrix interaction [229].




(a) Coir-HDPE.

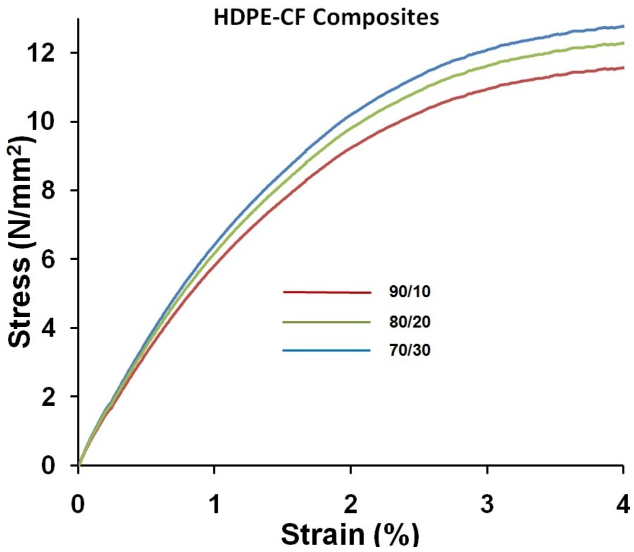



(b) Coir-HDPE-MAPE.

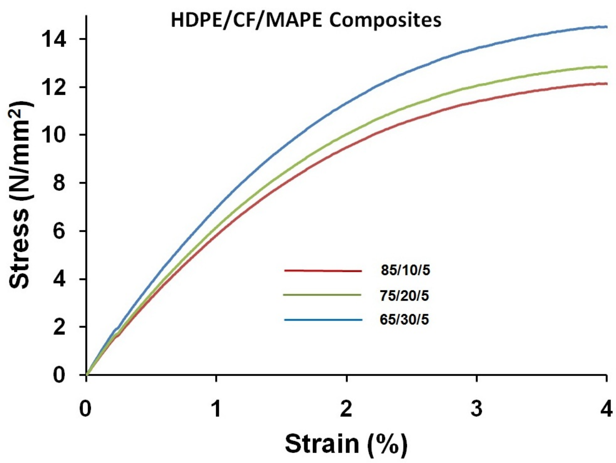



(c) Lime sludge-Coir-HDPE-MAPE

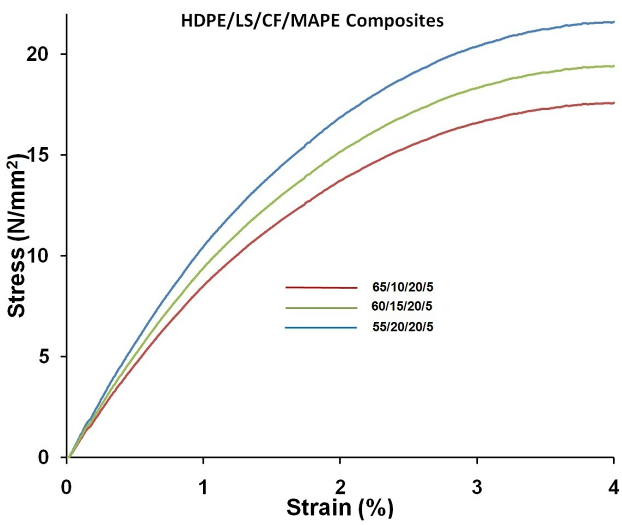
**Figure 6.9:** Sample stress-strain curves for coir-HDPE, coir-HDPE-MAPE and lime sludge filled coir-HDPE-MAPE derived after tensile testing.




(a) Coir-HDPE.




(b) Coir-HDPE-MAPE.




(c) Lime sludge-Coir-HDPE-MAPE

**Figure 6.10:** Sample stress-strain curves for coir-HDPE, coir-HDPE-MAPE and lime sludge filled coir-HDPE-MAPE derived after flexural testing.

Moreover, addition of rigid lime sludge particles increased the tensile modulus from 321.5 MPa to 378.6 MPa when filler loading increased from 10 to 20 wt %, thus increasing the rigidity of the composites. This increase in the strength and rigidity, led to the decrease in the ductility as the elongation at break decreased from 52.43 % to 24.93 % with increase in filler content. This may be attributed to particle agglomeration at higher filler content, filler-filler interaction rather than filler-matrix interaction, low ductility of particles and fibre bundling at higher weight fractions [229].

The flexural properties also improved with the addition of lime sludge particles in the composites. The flexural strength increased from 17.55 MPa to 21.56 MPa and the flexural modulus increased from 437.3 MPa to 475.7 MPa as the filler loading increased from 10 to 20 wt %. The strength and rigidity of the coir-HDPE-MAPE composites subjected to bending, increased with the addition of rigid lime sludge particles. This increment in the bending strength and rigidity may be attributed to the restriction in polymer chain mobility upon application of bending load [184, 227]. The Izod impact strength decreased from 20.69 J/m to 18.14 J/m upon addition of lime sludge particles to the coir-HDPE-MAPE composites (as the lime sludge content increased from 10 to 20 wt %). The presence of rigid particles make the failure mode of the composites more brittle and hence, relatively lower energy is absorbed upon impact loading even if the composites have good interfacial adhesion [155].

It is interesting to note that lime sludge addition improved most of the mechanical properties (*viz.* tensile strength, tensile modulus, flexural strength and flexural modulus) of the coir-HDPE-MAPE with the exception of elongation at break and impact strength, when compared with coir-HDPE-MAPE composites without any lime sludge addition. This suggests that rigid lime sludge particles had converted the coir-HDPE-MAPE composites into more rigid and less ductile material which resulted decrease in the elongation and impact strength. However, improvement in the overall mechanical properties indicate that lime sludge is an effective reinforcing agent in improving the strength and rigidity of the composites under both tensile and bending loads.

## 6.4 Lime sludge filled epoxy composites

Epoxy resin is a commonly used structural and adhesive material which exhibits properties such as high strength, tensile modulus, better insulation etc. However, epoxy resin has certain limitations in the sense that it is overly fragile [144]. Various studies have been conducted over the years in order to improve its properties by adding fillers and reinforcing agents in the epoxy matrix. Since industrial lime sludge waste is used as a filler in thermoplastic polymeric matrix (*viz.* HDPE) in this research (the properties of which has been illustrated in the previous sections), it is imperative that properties of lime sludge waste as a filler in a thermosetting plastic (*viz.* epoxy) also needs to be studied in order to understand the behaviour of lime sludge as filler in a thermosetting polymeric matrix.

In order to determine the effect of lime sludge weight % on the mechanical properties of lime sludge-epoxy composites, four types of samples with lime sludge content of 3, 6, 9 and 12 wt % are tested and compared with that of pure epoxy. The tensile properties of these samples are tabulated in Table 6.7. Sample stress-strain curves for lime sludge filled epoxy composites is shown in Fig. 6.11. It is observed that the tensile strength of pure epoxy is very low (3.748 MPa). However, the tensile strength increases as the weight % of lime sludge increase up to 6 wt % (8.625 MPa) indicating that lime sludge acts as effective reinforcement up to 6 wt %. Further increase in lime sludge wt % results in decrease in the tensile strength values which may be attributed to low interfacial adhesion at the filler-matrix boundary and lime sludge particles acting as stress concentration sites.

Addition of rigid particles improved the rigidity of the composites within the elastic limit resulting in an increase in the tensile modulus from 374 MPa for pure epoxy to 493 MPa for 12 wt % lime sludge added in the epoxy matrix. This is a common trend observed in particulate composites. Upon addition of filler particles, a mechanical restraint is introduced which resists deformation due to an applied load. Additionally, all the samples exhibited brittle failure, *i.e.* as the lime sludge wt % increases, the strain rate to failure decreases; resulting in the decrease in the ductility of the composites from 5.02 % for pure epoxy to 2.06 % for 12 wt % filler loading. This may be attributed to interfacial dewetting at the filler-matrix boundary and low ductility of rigid particulate fillers.

**Table 6.7:** Tensile properties of lime sludge filled epoxy composites

| Designation | Tensile strength (MPa) | Tensile modulus (MPa) | Elongation at break (%) |
|---|---|---|---|
| Pure Epoxy | 3.72±0.18 | 374.0±12.8 | 5.02±0.15 |
| 3LS-97 Epoxy | 4.83±0.23 | 400.0±9.5 | 4.80±0.15 |
| 6LS-94 Epoxy | 8.45±0.16 | 426.0±10.7 | 4.62±0.14 |
| 9LS-91 Epoxy | 6.37±0.11 | 456.0±11.5 | 3.20±0.13 |
| 12LS-88 Epoxy | 3.68±0.15 | 493.0±11.5 | 2.06±0.12 |

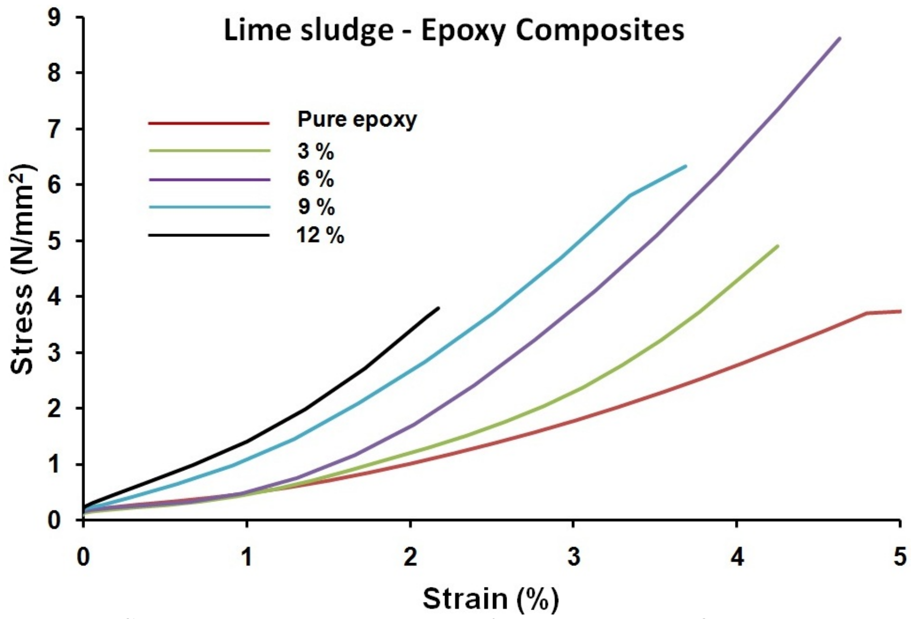



**Figure 6.11:** Sample stress-strain curves for lime sludge filled epoxy composites derived after tensile testing.

## 6.5 Lime sludge filled coir fibre epoxy composites

The overall mechanical properties of lime sludge filled epoxy composites are observed to be poor for them to be used in diverse applications. Hence, off late a substantial amount of research on hybrid composites with a variety of filler-fibre combinations have been conducted *viz.* bio particles-coir [204], crab carapace-coir [201], powdered hazelnut shells-jute [160] etc. in various polymer matrices. This is done in order to reap the benefits of both the reinforcing agents which would improve the overall properties of the composites. In this study, lime sludge waste is used as a filler in coir-epoxy composites in order to determine whether lime sludge addition in these composites offer a positive gain on the already existing counterparts. Two types of coir fibres are used in this study - (1) 30 wt % of randomly dispersed short coir fibre (8 mm long), and (2) 30 wt % of long coir fibre uniaxially aligned (120 mm long). Moreover, lime sludge content is varied as 0, 3, 6, 9, and 12 wt % in the composites.

### 6.5.1 Mechanical properties

Tensile and flexural properties of lime sludge filled short and long coir fibre composites are studied. An already known fact is that the tensile characteristics of long fibre composites exhibit significantly higher properties when the fibres are aligned in the direction of tensile loading due to effective stress transfer from the matrix to the fibres and the continuity of the fibres throughout the composites. Hence, it is expected that the long coir fibre composite would show superior properties than short fibre composites in the present case as well. The tensile and flexural properties of lime sludge filled short and long coir fibre reinforced epoxy composites are tabulated in Table 6.8.

#### 6.5.1.1 Tensile properties

The tensile and flexural properties of lime sludge filled short and long coir fibre reinforced epoxy composites are depicted in Fig. 6.13 and Fig. 6.14 respectively. Sample stress-strain curves obtained after tensile testing are provided in Fig. 6.12. Presence of a toe region in the initial parts is observed in stress-strain plots of the composites. This is present due to the fact that initially the coir fibres align and extend in the loading direction, upon application of load as if it were an uncoiling spring. This causes an initial increase in the value of strain upon the application of only small (negligible) amount of stress. As deformation leaves the toe region in the stress-strain curve, the response enters a nearly linear domain of substantial stiffness whereby the stress strain relation becomes linearly elastic. Finally, it enters the plastic region which is again very small due to the inherent stiffness and brittleness of the composite and epoxy resin.

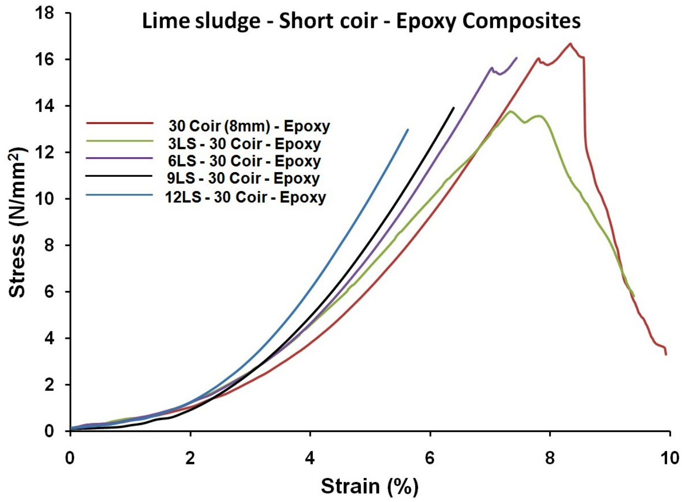
It is observed that initially the tensile strength increased upon addition of lime sludge for both short and long coir-epoxy composites. This suggests that lime sludge acts as an effective reinforcement and a resistance is exerted by these particles to the propagation of the initiated cracks up to a concentration of 6 wt %. This may be attributed to better dispersion of fibres and lime sludge particles in the matrix which ensured effective stress transfer from the matrix to the fibres and particles. Thus, appropriate dispersion and better adhesion at the filler-matrix interface results in increase in the tensile strength. However, as the lime sludge content increases beyond 6 wt %, the tensile strength starts to decrease due to particle agglomeration, poor dispersion of fillers, coir fibre bundling and low interfacial adhesion. This is in agreement with the results obtained by Aldousiri et al. [14], where it was reported that the tensile strength of fibre reinforced HDPE composites depended on factors such as filler loading and interfacial adhesion at the filler-matrix boundary. Additionally, it is natural that the long coir fibre composites exhibit better tensile properties than the short fibre composites as the long coir fibres are aligned in the direction of tensile loading which ensures effective stress transfer from the matrix to the fibres.

Addition of rigid lime sludge particles and fibres to a softer matrix leads to an increase in the tensile modulus with increasing lime sludge wt %. Thus, the tensile modulus increased from 411.3 MPa for 0 wt % to 543.2 MPa for 12 wt % lime sludge loading for short coir fibre composites and 501.4 MPa for 0 wt % to 613.2 MPa for 12 wt % lime sludge loading for long coir fibre composites. Needless to say, the rigidity of long fibre reinforced composites are found to be higher than that of short fibre composites owing to the fact that long, continuous and uniaxially aligned fibres are stiffer and stronger than short randomly distributed coir fibre in the epoxy matrix which provided effective stress transfer from the matrix to the fibres.

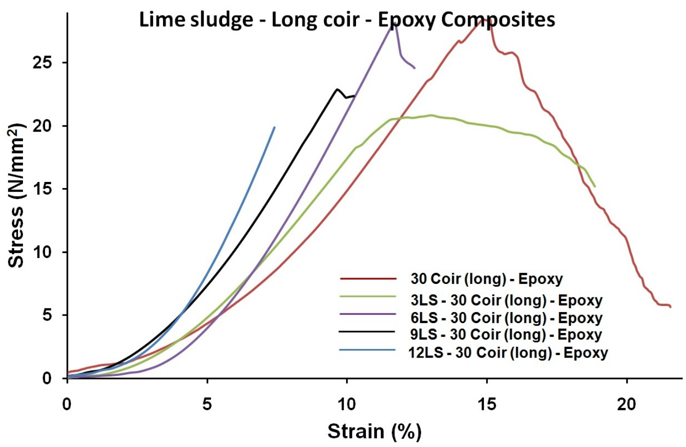
The ductility decreased with increasing filler content for both short and long coir fibre reinforced epoxy composites. The elongation at break (%) decreased from 10.14 % for 0 wt % to 6.17 % for 12 wt % lime sludge loading for short coir fibre composites and 21.26 % for 0 wt % to 7.55 % for 12 wt % lime sludge loading for long coir fibre composites. This decline in the ductility of composites is a characteristic of most reinforced polymeric composites. This is a consequence of low elongation of fibres and rigid lime sludge particles which restricts the flow of polymer molecules past one another. Such trend in the decrease in the ductility of composites with increasing filler content was also reported earlier by Yao et al. [273] for PP composites filed with $CaCO_3$ and shell waste. Thus, tensile properties of lime sludge filled coir-epoxy hybrid composites are found to be much better than pure epoxy due to the benefits of adding both lime sludge and coir fibres in the polymeric matrix. At higher filler content in excess of 6 wt %, particle agglomeration could lead to the formation of micro voids acting as stress raisers; thus decreasing the tensile properties.Such trend in the tensile behaviour of clay filled coir reinforced polymeric composites were reported earlier by Muthu et al. [167]

#### 6.5.1.2 Flexural properties

The flexural strength increased from 30.66 MPa for 0 wt % to 45.88 MPa for 12 wt % lime sludge loading in case of short coir fibre composites and 42.68 MPa for 0 wt % to 60.42 MPa for 12 wt % lime sludge loading in case of long coir fibre composites. Sample stress-strain curves obtained after flexural testing are provided in Fig. 6.15. It is observed that the flexural strength increased with increase in the lime sludge filler content in the composites. This is due to the efficient reinforcing effect of lime sludge particles along with the coir fibres. Additionally, as reported in previous studies, increase in the flexural strength may also be attributed to high mechanical anchorage of the matrix provided by rough lime sludge particles and coir fibres, in addition to better stress transfer at the filler-matrix interface under

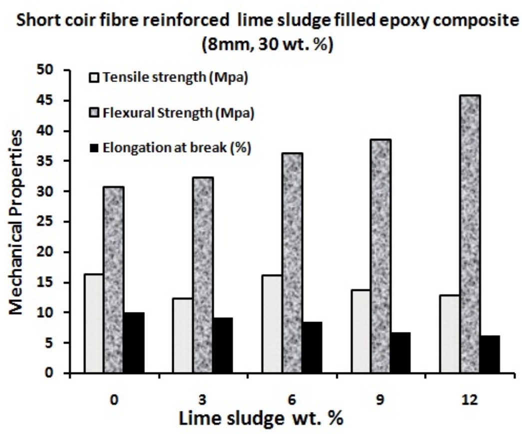



(a) Short coir composites.

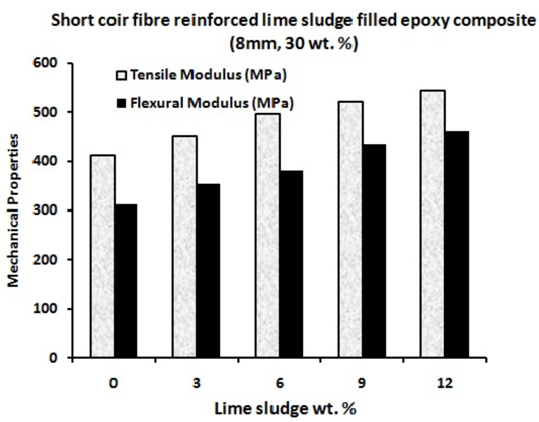



(b) Long coir composites.

**Figure 6.12:** Sample stress-strain curves for lime sludge filled short and long coir fibre reinforced epoxy composites derived after tensile testing.

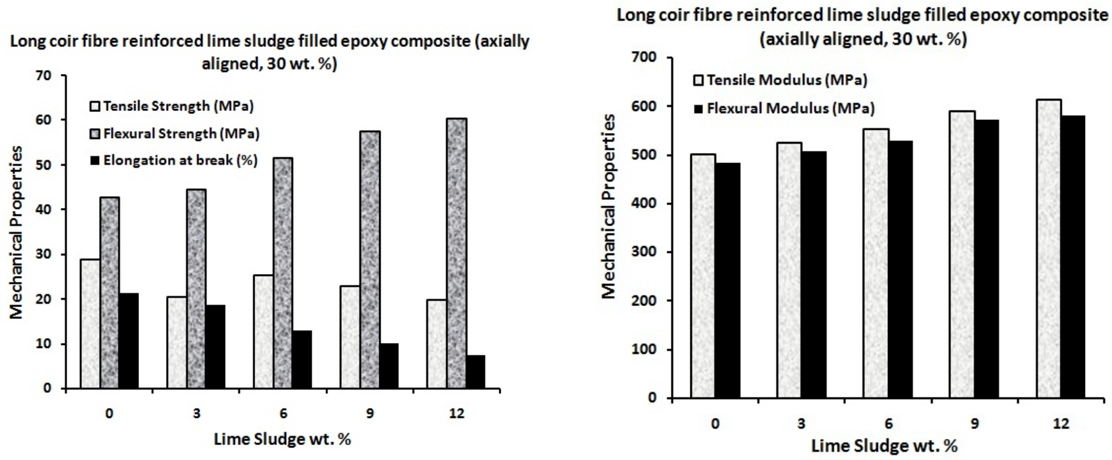



(a)




(b)

**Figure 6.13:** Mechanical properties of lime sludge filled short coir fibre reinforced epoxy composite.




(a) (b)

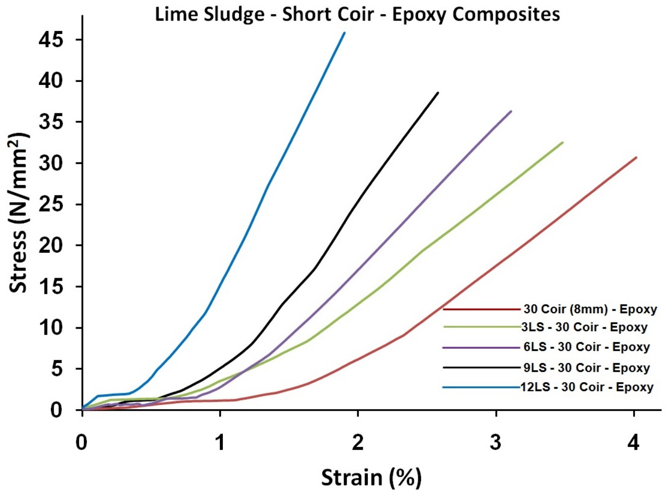
**Figure 6.14:** Mechanical properties of lime sludge filled long coir fibre reinforced epoxy composite.

bending stresses [124, 131, 141].

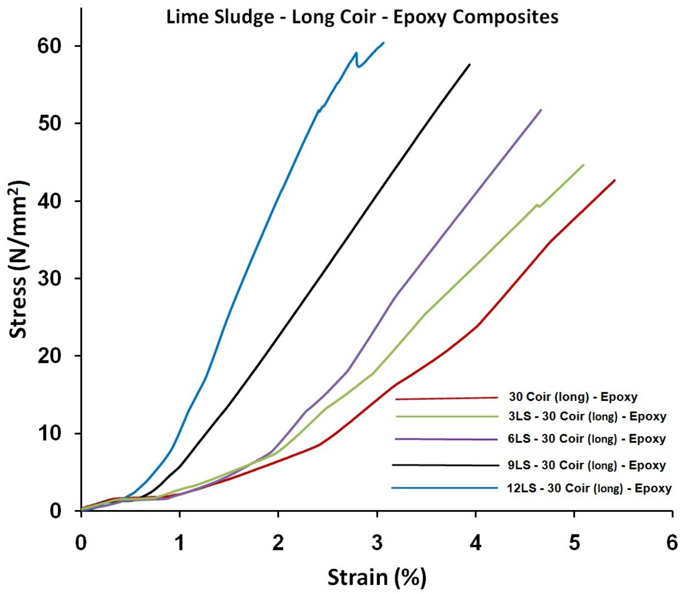
Flexural modulus increased with increasing lime sludge loading in the composites. The increase in flexural modulus follows a similar trend to tensile modulus, which can be attributed to the enhanced brittleness and stiffness of the composites. Incorporation of rigid particulate filler and fibres, improved the stiffness (flexural modulus) of the polymeric composites under bending stresses. Higher concentration of rigid materials demands higher stress for the same amount of deformation and hence the increase in the flexural modulus. This increase in the flexural modulus and strength with increasing filler loading was also obtained from various studies conducted previously [124, 131, 141]. Although the mechanical behavioural trend is similar to short fibre composites, it is observed that both flexural strength and modulus of continuous (long) fibre composites are much higher than short fibre composites for the same filler loading. Continuous fibres provide effective reinforcement and better stress transfer from matrix to the fibres upon loading, hence they show better flexural properties than short fibre composites.

### 6.5.2 Thermal properties

Thermal parameters such as thermal degradation and % residual weight left at 500 °C are used in order to study the effect of lime sludge on the thermal properties of coir - epoxy composites. TGA curves are plotted for 3 and 9 wt % lime sludge added coir fibre - epoxy composites. The results calculated from the TGA thermograms are shown in Fig. 6.16. In case of lime sludge filled coir epoxy composites, the




(a) Short coir composites.




(b) Long coir composites.

**Figure 6.15:** Sample stress-strain curves for lime sludge filled short and long coir fibre reinforced epoxy composites derived after flexural testing.

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 $CaCO_3$; 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 % lime sludge filled coir-epoxy composites at 500 °C is due to the

**Table 6.8:** Tensile properties of lime sludge filled coir epoxy composites

| Designation | Tensile strength (MPa) | Tensile modulus (MPa) | Elongation at break (%) | Flexural strength (MPa) | Flexural modulus (MPa) |
|---|---|---|---|---|---|
| 30 Coir - Epoxy (8mm) | 16.27±0.12 | 411.4±15.3 | 10.14±0.14 | 30.66±0.27 | 312.2±10.3 |
| 3LS -30 Coir - Epoxy (8mm) | 12.33±0.11 | 451.6±13.6 | 9.18±0.16 | 32.27±0.24 | 353.4±11.1 |
| 6LS - 30 Coir - Epoxy (8mm) | 16.19±0.17 | 496.0±14.6 | 8.55±0.25 | 36.28±0.22 | 379.8±12.3 |
| 9LS - 30 Coir - Epoxy (8mm) | 13.76±0.26 | 521.0±12.8 | 6.74±0.21 | 38.57±0.19 | 434.2±8.5 |
| 12LS -30 Coir - Epoxy (8mm) | 12.91±0.15 | 543.4±11.9 | 6.17±0.18 | 45.88±0.31 | 460.4±10.9 |
| 30 Coir - Epoxy (long) | 28.91±0.75 | 501.6±14.6 | 21.26±0.23 | 42.68±0.20 | 484.0±12.5 |
| 3LS -30 Coir - Epoxy (long) | 20.41±0.43 | 524.0±18.8 | 18.76±0.18 | 44.46±0.15 | 507.8±13.3 |
| 6LS - 30 Coir - Epoxy (long) | 25.42±0.39 | 552.6±10.1 | 12.88±0.29 | 51.69±0.22 | 528.4±13.5 |
| 9LS - 30 Coir - Epoxy (long) | 22.95±0.77 | 587.4±18.7 | 10.11±0.15 | 57.54±0.19 | 572.4±8.6 |
| 12LS -30 Coir - Epoxy (long) | 19.72±0.23 | 613.2±12.0 | 7.56±0.38 | 60.42±0.21 | 581.4±11.9 |

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 % lime sludge filled coir-epoxy composites is due to the higher content of stable lime sludge present in the composite at that temperature. Thus, at higher temperature the weight loss percentage of 3 wt % lime sludge composite is found to be larger than the 9 wt % lime sludge composite due to presence of higher non-decomposed lime sludge in the latter case. This suggests that as the amount of lime sludge increases, the composites become thermally more stable.

## 6.6 Summary

In order to be commercially viable and structurally feasible as a filler in polymeric composites, an industrial waste must be versatile enough to improve the properties of different types of composites - with a variety of polymeric matrices and reinforcing agents. Hence in this chapter, lime sludge waste is used as a filler in a variety of matrices *viz.* HDPE-PP blends, HDPE-MAPE, MAPE and epoxy, and also used alongside coir fibres in a polymeric matrix. The summary of the chapter is as follows:

- **Lime sludge filled HDPE-PP blends**: It is observed that lime sludge particles decreased the overall tensile strength of the composites when compared with virgin PP and HDPE, due to factors such as low interfacial bonding and high stress concentration sites induced by the rigid particles. However among

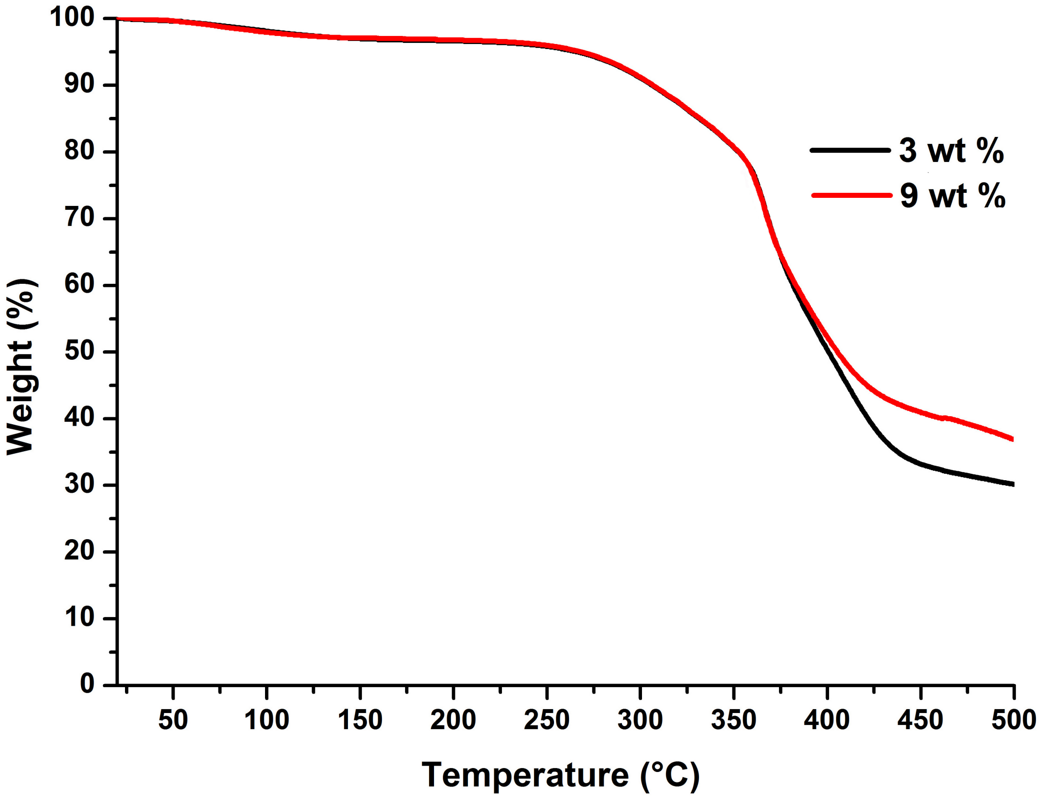



**Figure 6.16:** TGA thermograms of 3 wt % and 9 wt % lime sludge filled coir-epoxy composites.

the composites, the tensile strength increased with increasing filler content of 20 wt %, indicating effective reinforcement of lime sludge particles. Rigid lime sludge particles improved the rigidity and hardness of the composites while the ductility (elongation) decreased as a result of it.

DSC analysis revealed that lime sludge addition increased the onset and melting temperatures of both HDPE and PP while decreasing the melting enthalpy, thus indicating that lesser heat is required for extrusion and molding (advantage). TG analysis showed that the rise in the thermal stability of lime sludge filled HDPE-PP blends may be attributed to the addition of lime sludge. This idea is also reinforced by the fact that the residual weight % of the composites increased with increasing lime sludge content.

- **Lime sludge filled HDPE-MAPE composites**: MAPE compatibilizer added to lime sludge filled HDPE composites improved the overall mechanical properties of the composites when compared to raw or stearic acid coated lime sludge filled HDPE composites, due to enhanced adhesion at the filler-matrix boundary. The properties increased with increasing MAPE content in the composite (up to 5 wt % MAPE). The tensile strength increased up to 20 wt % lime sludge in the HDPE-LS-MAPE composites indicating effective reinforcement, but decreased thereafter due to particle agglomeration. The tensile and flexural modulus increased upon addition of MAPE, coir fubre and rigid filler particles which also resulted in a decrease in the ductility (elongation). The flexural and impact properties also improved due to MAPE addition on account of better adhesion at the interfacial boundary.

- **Lime sludge filled coir-HDPE-MAPE hybrid composites**: The overall mechanical properties of the composites improved upon addition of short coir fibres randomly dispersed in the HDPE matrix. A 5 wt % MAPE addition enhanced the adhesion at the filler-matrix interface, thereby also improving the properties of the composites. Lime sludge and coir fibres proved to be an effective reinforcing agents up to 15 wt % and 20 wt % respectively, beyond which the strength decreased due to particle agglomeration, interfacial dewetting and coir fibres bundling. Evidently, the rigidity and impact strength of the composites increased due to addition of rigid particles, coir fibres and MAPE compatibilizer. However, this also caused a decrement in the ductility of the composites.

- **Lime sludge filled coir-epoxy hybrid composites**: The overall mechanical properties of the epoxy composites improved upon addition of short coir fibres randomly dispersed in the epoxy matrix. Needless to say, the long fibre composites showed better properties than the short ones due to better stress transfer from the matrix to the long fibres and the ability of fibres to endure more load being aligned in the loading direction. The role of lime sludge particle is similar to that shown in case of the other composites tested before. The rigidity (tensile and flexure) increased at the expense of ductility (elongation). The flexural strength increased due to ability of filler particles and coir fibres to act as effective reinforcing agents under bending stresses. However, the tensile strength increased only up to 6 wt % filler, beyond which particle agglomeration, poor dispersion of fillers, coir fibre bundling and low interfacial adhesion cause a decrease in tensile strength.