# Chapter 4

# Raw lime sludge filled HDPE composites

In this chapter, the analysis of the raw lime sludge collected from the dumpyard of a paper mill is described, which involves determining the constituents in lime sludge through various characterization techniques and assessing its thermal stability. Additionally, this chapter also discusses the feasibility of using lime sludge as reinforcing filler in HDPE composites, thus integrating two advantages - (i) the scientific value - utilization of industrial lime sludge waste thereby decreasing pollution, and (ii) commercial value - reducing the manufacturing cost of polymeric composites and increasing the viability of the industrial waste. Hence, this chapter illustrates the characteristics of HDPE composites filled with increasing weight fraction of lime sludge; thereby exploring the effects of lime sludge on the mechanical, thermal, and morphological properties of the composite in comparison to pure HDPE. 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.

## 4.1 Characterization of lime sludge

Lime sludge collected from Jagiroad Paper Mill, Assam(India) is characterized using XRD, ICP-OES and TGA analysis in order to determine the structure, composition and thermal properties of lime sludge.

### 4.1.1 SEM Analysis

Fig. 4.1 shows the secondary electron micrograph of lime sludge powder after compounding, which depicts the particle size of lime sludge powder. Random lime sludge particles are measured in the SEM micrograph to assess the size of the lime sludge particles. It is observed from the micrograph that the size of a lime sludge powder particle is less than or equal to 2 $\mu$m. Incorporation of lime sludge particles of a particular size to the polymer matrix will play a pivotal role in increasing or decreasing the mechanical properties. Larger the particle size, higher is the stress concentration at these particle sites, and hence, greater is the chance of crack initiation and propagation under loading conditions; thus causing premature failure and a decrease in the mechanical properties.

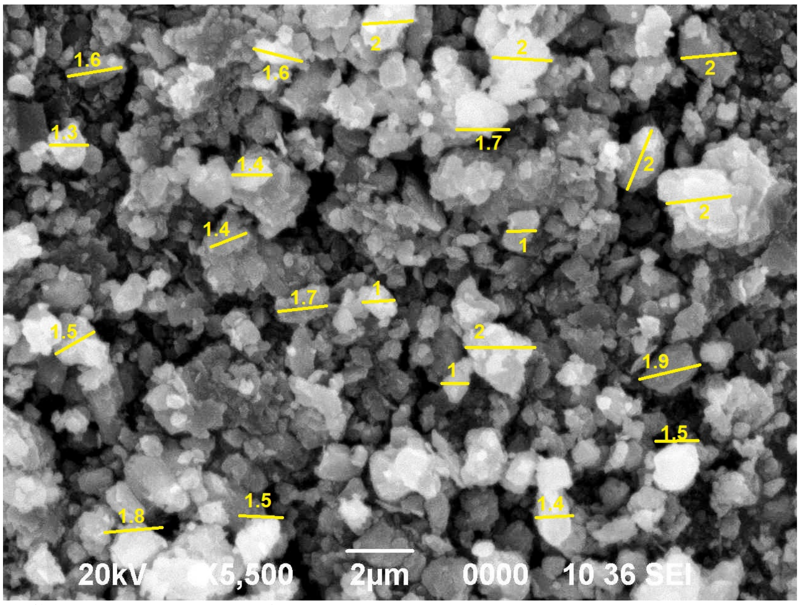


**Figure 4.1:** SEM micrograph of raw lime sludge powder depicting its average particle size.

### 4.1.2 XRD Analysis

The crystal pattern of the lime sludge powder obtained through powder XRD technique is shown in Fig. 4.2. It is observed that the main diffraction peaks of the crystalline phases present in lime sludge are in the range of 20°- 60°. It is a known fact that $CaCO_3$ is characterized by three crystalline phases: calcite, aragonite, and vaterite [77]. The experimental XRD data of lime sludge obtained in the present study showed striking resemblance with the diffraction peaks of calcite obtained from JCPDS card 5-586. The most prominent peak of calcite observed in the XRD pattern is located at 29.4° corresponding to the (1 0 4) reflections from the calcite crystals structure. Additionally, calcite peaks are observed at 23.05°, 36°, 39.4°, 43.15°, 47.5°, 48.55°, 56.6° and 57.45°. These peaks conformed well to the diffraction data of calcite in terms of locations of peaks and their relative intensities. Hence, the observed diffraction data showed the presence of $CaCO_3$ in lime sludge in the form of calcite. However, the presence of certain other peaks in different locations of the diffraction pattern is due to the fact that lime sludge also contains other inorganic compounds in small quantities. Therefore, XRD validates that $CaCO_3$ in lime sludge is mainly present in the form of calcite crystals, and this makes lime sludge an ideal material as a reinforcing agent in polymeric matrices.

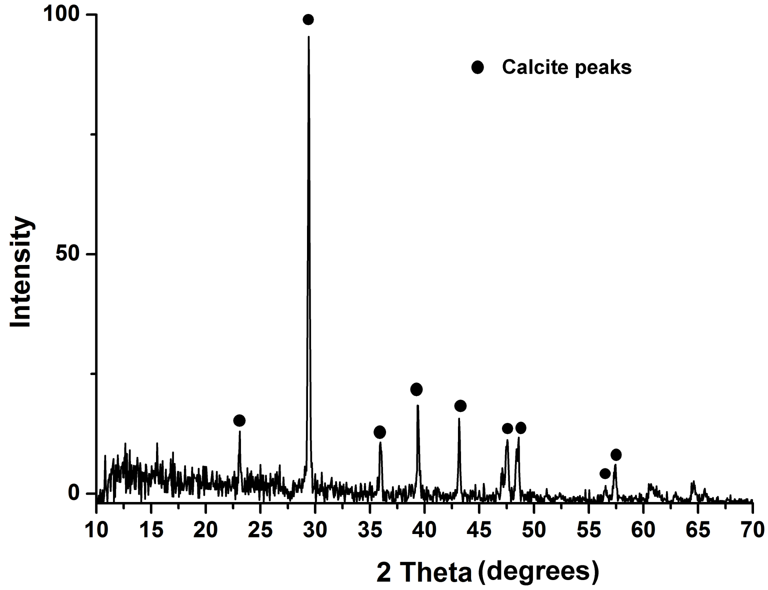


**Figure 4.2:** XRD crystal pattern for raw lime sludge powder.

### 4.1.3 ICP-OES Analysis

Elemental analysis of lime sludge done by ICP-OES is shown in Table 4.1. Elemental analysis showed a calcium concentration of 514.5 ppm which is in close conformation with that obtained by Deka and Yasmin [67] in an earlier study on lime sludge obtained from same Jagiroad Paper Mill, Assam (India). Additionally, they also reported that the percentage of $CaCO_3$ in the lime sludge to be 66.5% with a water-holding capacity of 70.4% along with a few other trace elements. From this analysis, it is evident that lime sludge mainly consists of $CaCO_3$ as the main constituent with traces of a few other compounds. Moreover, magnesium is the next prominent constituent in lime sludge which is present in the form of talc or magnesium carbonate ($MgCO_3$), derived from paper fillers, coating pigments, and coagulants used in papermaking and process effluent treatments [132]. It is a known fact that $CaCO_3$ is the most widely used filler in polymeric composites; while it has been reported earlier that $MgCO_3$ act as flame retardants when used as fillers in polymeric composites [207]. Hence, lime sludge consisting of mainly $CaCO_3$ in addition to some amount of $MgCO_3$ which has the potential to contribute positively as a reinforcing filler in polymeric composites.

**Table 4.1:** ICO-OES analysis of lime sludge showing elemental concentrations in ppm.

| S. No. | Element | Concentration (ppm) |
|---|---|---|
| 1 | Ca | 514.5 |
| 2 | Fe | 28.8 |
| 3 | Al | 51.7 |
| 4 | Mg | 285.2 |

### 4.1.4 TG Analysis

Thermal degradation of lime sludge is studied using TGA up to a temperature of 600 °C. The weight loss % of lime sludge with increase in the temperature is shown in Fig. 4.3. Thermal degradation of lime sludge is studied using TGA up to a temperature of 600 °C. It is observed that there is hardly any loss in the weight percent of the lime sludge sample up to 600 °C. A small loss of 7.8 wt% is detected which may be attributed to loss of strongly physically adsorbed water between 40 °C and 110 °C and loss of water associated with magnesium hydroxide between 200 °C and 400 °C [28]. This is in stark difference with the thermal analysis of paper sludge

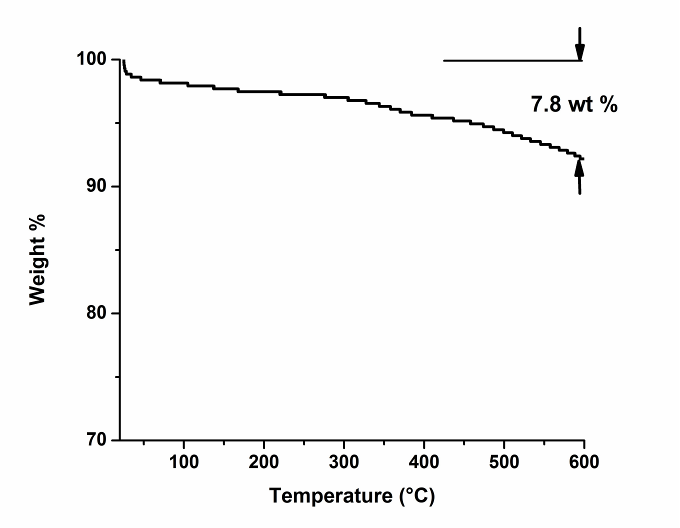


**Figure 4.3:** TGA curve showing the degradation process of lime sludge up to 600 °C.

done by Son et al. [244] which showed the degradation of cellulosic fibers from paper sludge at higher temperatures, thus leaving behind only the inorganic contents. Hence, the TGA plot of lime sludge with only a small weight loss of 7.82% indicates the absence of any organic matter (cellulosic fibers) in the lime sludge. It is also provided in the technical report by Baker et al. [28] that upon further heating, the loss between 650 °C and 800 °C is due to carbon dioxide being driven off, while $CaCO_3$ gets decomposed.

## 4.2 Lime sludge-HDPE composites

It is imperative to mention that the properties of lime sludge-HDPE composites needs to be studied in detail in order to assess the feasibility of using industrial lime sludge waste as filler or reinforcing agent in a polymeric composite. In the following sections, the mechanical, thermal and morphological properties of lime sludge-HDPE composites are discussed in comparison with pure HDPE.

### 4.2.1 Mechanical properties

Tensile, flexure, and Izod impact tests are conducted for pure HDPE and lime sludge filled HDPE composites (5, 10, 15, 20, 25, and 30 wt % lime sludge in polymer matrix) in order to determine the mechanical properties of the newly fabricated composites with increasing lime sludge additive in conjunction with the pure polymer. Since, $CaCO_3$ is commercially the most widely used filler in polymeric composites, the results observed for lime sludge-HDPE composites are compared with previously reported studies on the mechanical properties of pure $CaCO_3$ filled polymeric composites. This would provide a greater insight into the feasibility of using lime sludge waste in polymeric composites.

#### 4.2.1.1 Tensile strength

The variation in tensile strength with increasing filler loading is shown in Fig. 4.6(a). Sample stress-strain curves for HDPE and raw lime sludge filled HDPE with increasing weight fraction of lime sludge loading is shown in Fig. 4.4. Moreover, samples of lime sludge-HDPE composite after tensile test exhibiting higher and lower ductility based on their filler content is shown in Fig. 4.5. It is found that the tensile strength of pure HDPE is higher than that obtained from all the lime sludge - HDPE polymeric composites. There is a moderate drop in the tensile strength with increasing lime sludge filler loading. This is in conformation with the results obtained by Atikler et al. [20] for pure $CaCO_3$ filled HDPE composites wherein it was observed that the tensile strength decreased with increasing filler loading. The reason may be due to dewetting along the filler  matrix boundary may occur due to poor bonding between them. Another probable cause may be larger particle size of lime sludge causing sites of higher stress concentrations and subsequent void creation due to frictional pull out of particles, thereby decreasing the tensile strength [162]. Additionally, crazing in polymers is one of the important reasons for decrease in strength and subsequent fracture in polymers under tensile loading. $CaCO_3$ is known to promote craze formation in deformed polymers before fracture [141]. However, an increase of about 1.8 MPa in the tensile strength was observed as the filler loading increased from 5 wt % to 10 wt % (11.9 - 13.7 MPa) after which the tensile strength decreases again up to 30 wt % filler loading. Hence, lime sludge proves to be a better reinforcement up to 10 wt %, indicating better particle dispersion and filler-matrix bonding compared to those composites above 10 wt % filler content. This is evident from the SEM micrographs shown in Fig. 4.6(b) and (c) at the fractured surface of the composites for 10 and 30 wt % lime sludge additions, respectively. Fig. 4.6(b) shows that lime sludge particles remain embedded in the matrix depicting better filler-matrix bonding and particle dispersion at 10 wt % lime sludge loading. However, lime sludge particles tend to drop out of the matrix in 30 wt % lime sludge added composites as seen in Fig. 4.6(c) due to their poor interfacial bonding with the matrix. Additionally, there is also evidence of particle agglomeration in 30 wt % lime sludge composites where the sizes of particles (denoted by the black circles in Fig. 4.6(b) and (c)) are larger than that at 10 wt % lime sludge added composites. Larger particle size due to particle agglomeration at higher concentrations of lime sludge lead to higher stress concentration sites. Hence, poor filler-matrix bonding and particle agglomeration (higher stress concentration sites) can be attributed to the gradual decrease in the tensile strength at higher concentrations of lime sludge in the composites, *i.e.* at lime sludge weight fractions >10 wt %.

#### 4.2.1.2 Tensile modulus

A significant increment in the elastic modulus of composites with increasing filler content is observed, when compared with the lower modulus of pure HDPE. The variation in tensile modulus with increasing filler loading is shown in Fig. 4.7. There is a rise in the elastic modulus from 139.6 MPa for pure polymer to 215.2 MPa for 30 wt % lime sludge filled HDPE composite. This increasing trend is similar

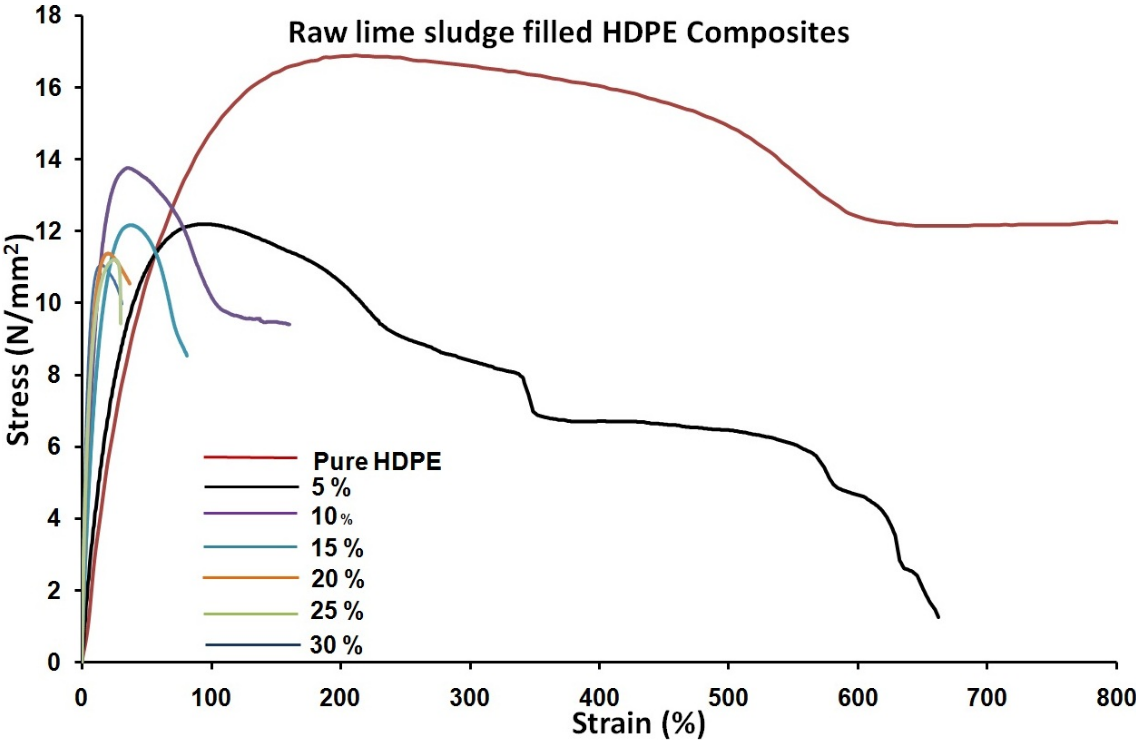


**Figure 4.4:** Sample stress-strain curves for HDPE and lime sludge filled HDPE composites derived after tensile testing.

**Figure 4.5:** Lime sludge-HDPE composite samples after tensile test having higher and lower ductility.

to that reported by Atikler et al. [20] which revealed that Young's modulus for 30 wt % pure $CaCO_3$ filled HDPE increased significantly when compared that that of HDPE alone. In the present case, the increase in Young's modulus for 30 wt % lime sludge-HDPE composite is about 1.5 times the value for pure HDPE, thus indicating that lime sludge particles provide more rigidity to the composites than pure $CaCO_3$. Since the modulus is measured before any significant plastic deformation took place, it is independent of the filler-matrix interactions, thereby making the effects of particulate shape and specific surface area immaterial in the measurement of elastic

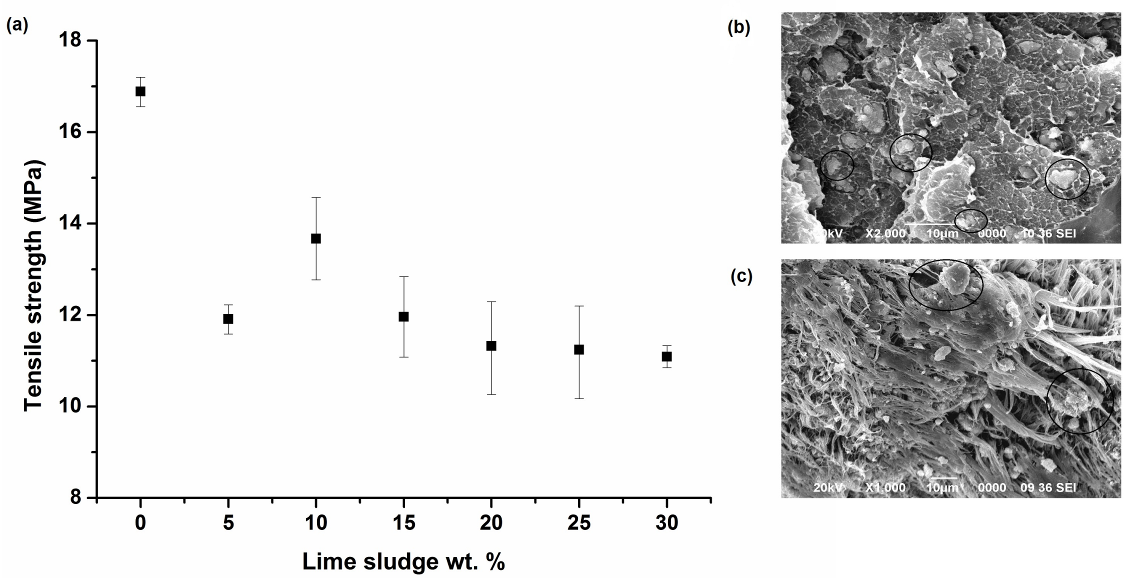


**Figure 4.6:** (a) Tensile strength variation in the composites as a function of lime sludge loading, (b)fractured surface of 10 wt % , (c) fractured surface of 30 wt % lime sludgeHDPE composite.

modulus. The rise in the elastic modulus is largely attributed due to the following reasons (a) replacement of the fully polymeric HDPE matrix with parts of rigid particulate fillers and (b) introduction of a mechanical restraint due to the restriction in deformation provided by the addition of particulate filler.

### 4.2.1.3 Elongation at break

Various weight fractions of lime sludge filled HDPE composite samples subsequent to tensile test is shown in Fig. 4.8 (depicting their ductility). It is observed that the elongation at break decreased significantly with increasing filler content which is a characteristic of particulate-reinforced thermoplastic composites as shown in Fig. 4.7. The decrement in the elongation at break (806% for pure polymer to 32.8% for 30 wt % lime sludge-HDPE composites) is due to the low elongation of filler that restricts the flow of polymer molecules past one another. This indicates that the mode of failure changes from ductile to brittle behavior with increasing filler loading. Rigidity of particulate fillers, filler agglomeration at higher wt % lime sludge filled composite, and deformation at selected stress concentration sites causing fracture at the at filler-matrix boundary may be attributed to lower elongation at break. Atikler et al. [20] also obtained a similar trend in the elongation % for $CaCO_3$-filled HDPE composite, wherein the elongation at break % decreased from a value greater than 1000% for pure HDPE to that less than 100% for 30 wt % $CaCO_3$ filled HDPE composite.

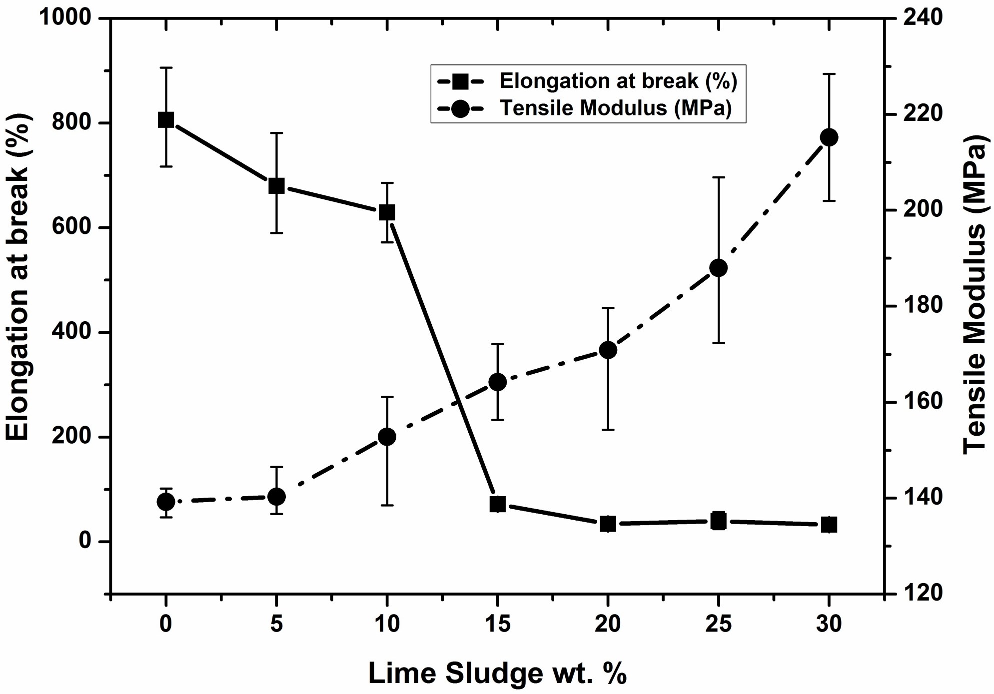


**Figure 4.7:** Variation in tensile modulus and elongation at break of composites with increasing lime sludge loading.

### 4.2.1.4 Flexural strength

The sample stress-strain curves for HDPE and raw lime sludge filled HDPE with increasing weight fraction of lime sludge loading derived after flexural testing is shown in Fig. 4.9. A sample lime sludge-HDPE composite before and after flexural test is shown in Fig. 4.10. Moreover, Fig. 4.11 shows increasing order of flexure strength with increasing filler loading (6.2 MPa for pure polymer to 12.2 MPa for 30 wt % lime sludge-HDPE composite) which confirms that lime sludge acts as a better reinforcement under flexural loading conditions. This indicates better stress transfer between the matrix and filler particles under bending stresses. The increment in flexure strength also indicated better surface properties for lime sludge filled composites since the flexural properties are sensitive to the surface of specimens. This is in conformation with the observed literature which reveal that the flexural properties of composites increase with increasing loading of rigid particulate fillers in a polymeric matrix [131, 141].

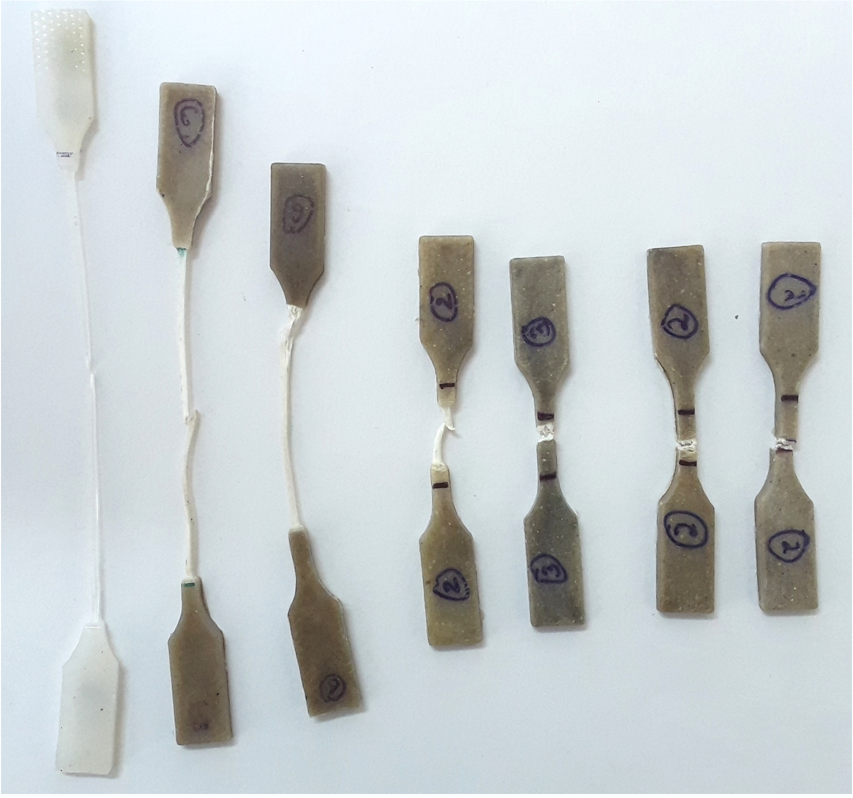


**Figure 4.8:** Lime sludge-HDPE composites after tensile test depicting elongation at break (from *left* to *right* with increasing wt % of lime sludge).

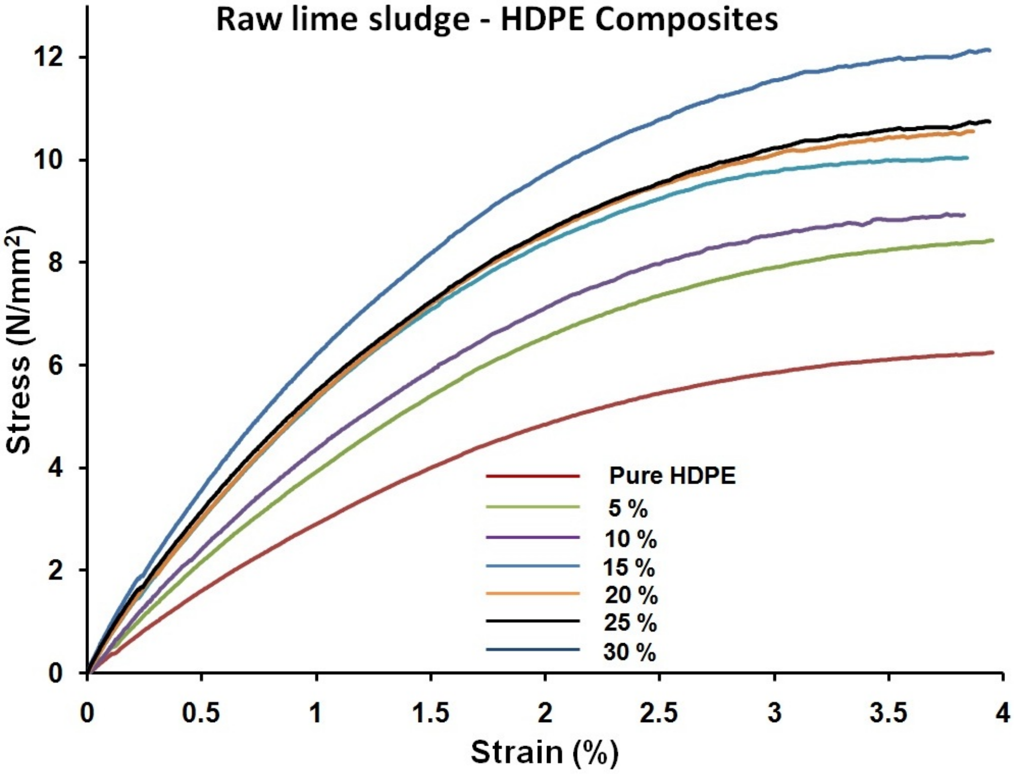


**Figure 4.9:** Sample stress-strain curves for HDPE and raw lime sludge filled HDPE composites derived after flexural testing.

**Figure 4.10:** A lime sludge filled HDPE composite before and after flexural (bending) test.

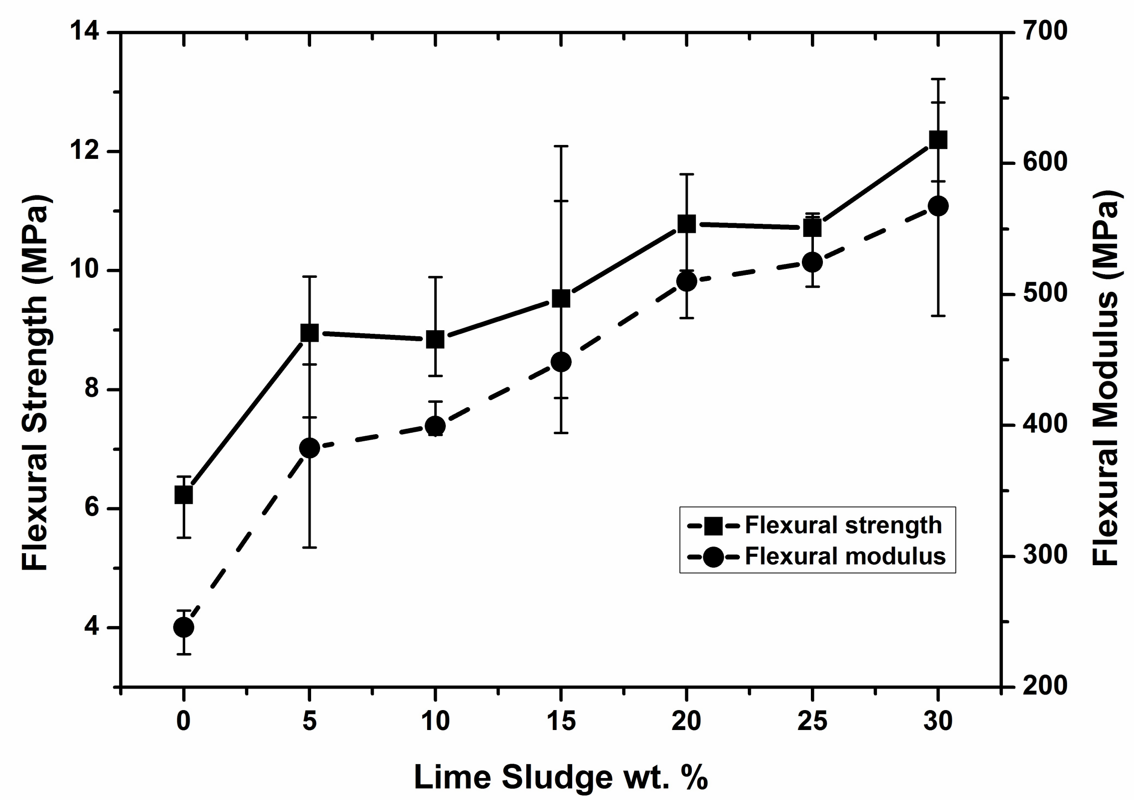


**Figure 4.11:** Variation in flexural strength and flexural modulus of composites with increasing lime sludge loading.

#### 4.2.1.5 Flexural modulus

As shown in Fig. 4.11, incorporation of rigid particulate filler such as lime sludge improved the stiffness of the polymeric composites which resulted in an almost linear increment of flexural modulus (245.7 MPa for pure polymer to 567.5 MPa for 30 wt % lime sludge-HDPE composites) similar to the tensile modulus. Higher concentration of rigid particulate materials demands higher stress for the same amount of deformation and hence the increase in the flexural modulus. Additionally, flexural modulus of composites is found to be lower than its tensile counterparts, the reason being the presence of excess polymer on the surface as a result of the restriction imposed by the mold walls during molding of the composites. Since the surface of specimens is at maximum stress during flexural analysis, the properties of the surfaces are emphasized more in this case, unlike tensile testing, where the bulk properties of the specimen in the loading direction are exposed.

#### 4.2.1.6 Impact Properties

A lime sludge filled HDPE composite before and after impact test is shown in Fig. 4.12. Parameters such as toughness properties of reinforcement, the nature of the interfacial region, and the nature of fracture in the matrix, highly influence the impact strength of a composite [48]. As shown in Fig. 4.13, it is observed that the impact properties decreased with the introduction of filler materials as compared to the pure HDPE samples (30.2 J/m for pure polymer to 7.35 J/m for 30 wt%). It is a well-known fact that the highest stiffness composites (high modulus of elasticity) exhibit the lowest impact resistance since high stress is transferred from the polymeric matrix to the filler particles [7, 208]. The particulate fillers act as points of stress concentration and anisotropic particle orientation throughout the composite restricts plastic deformation, thereby causing embrittlement of the composite. Upon impact, the crack propagates to the interfacial regions and the material fails in a brittle manner as it cannot plastically deform. However, a very low variation of impact strength was observed with increasing filler weight fractions.

**Figure 4.12:** A lime sludge filled HDPE composite before and after impact test.

It is observed that industrial lime sludge waste used as filler in HDPE provides comparable mechanical properties to both pure HDPE and $CaCO_3$-HDPE composites. Additionally, the rigid lime sludge particles provide better rigidity within the elastic limit than pure HDPE as is evident from the significant increase in

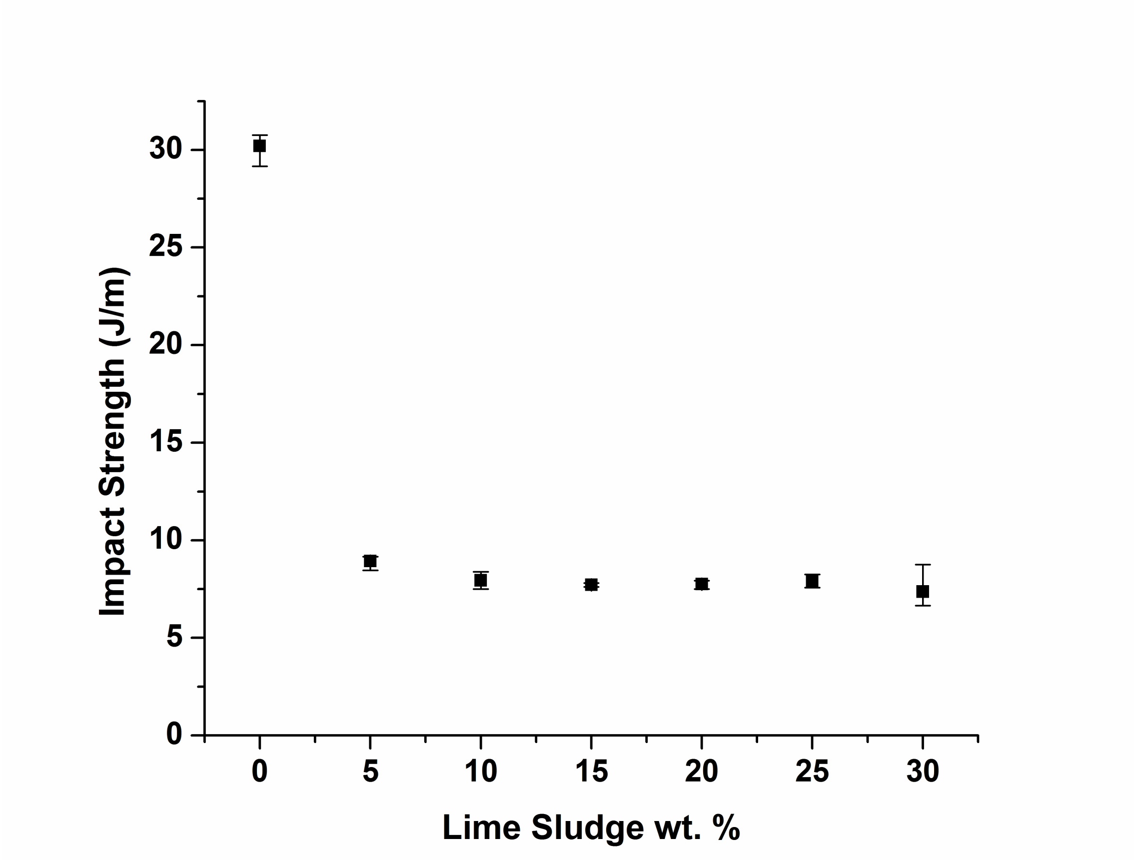
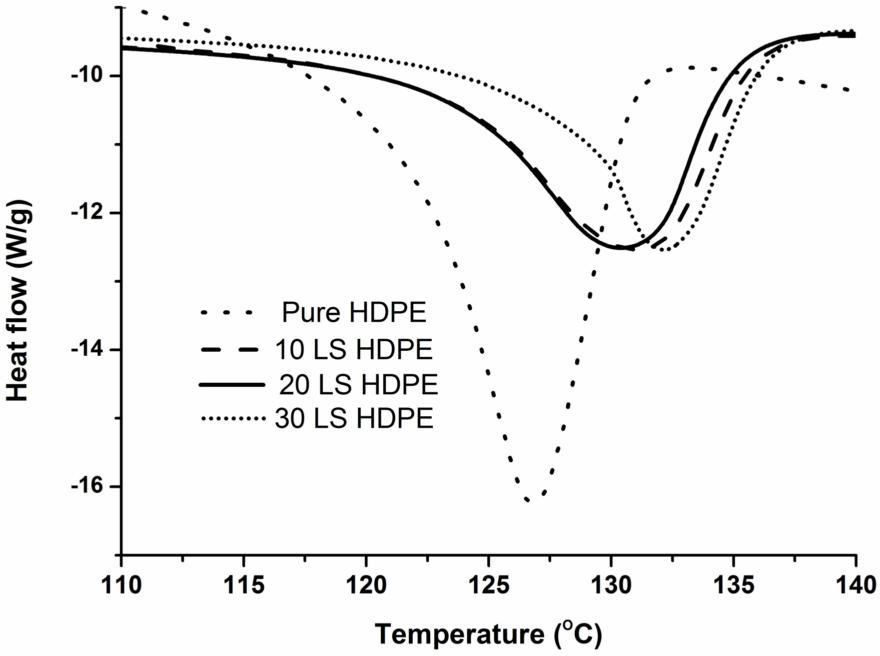


**Figure 4.13:** Variation in Izod impact strength of composites with increasing lime sludge loading.

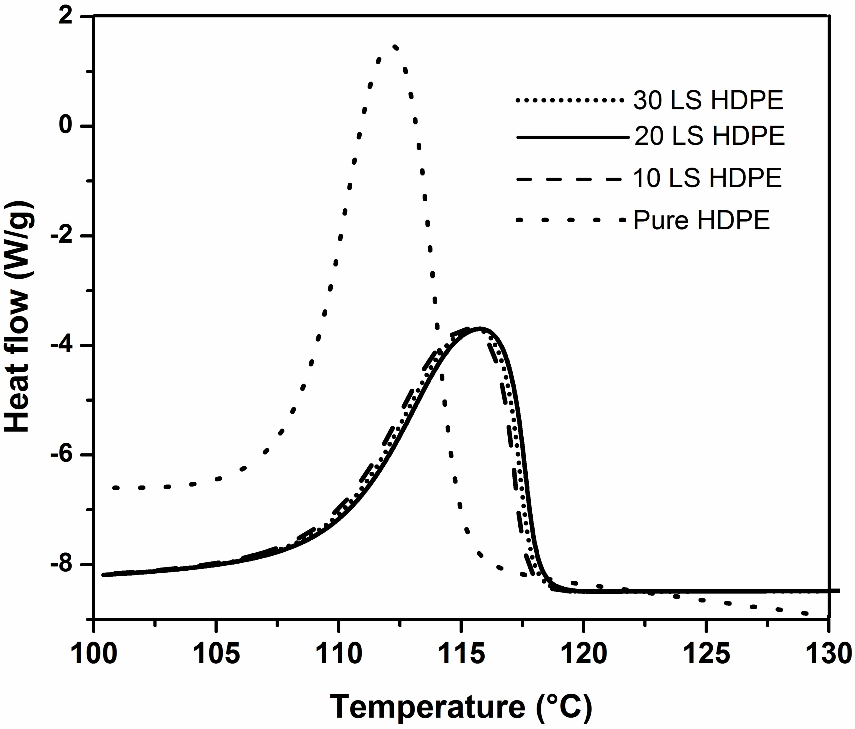
the Young's modulus and flexural modulus. Increment in tensile modulus, flexural strength and flexural modulus justifies lime sludge not only as a filler but also as a reinforcing agent in HDPE composites. Hence, industrial lime sludge waste may be used in a polymeric matrix which would increase the viability of an industrial waste and decrease the cost of the composites without much compromise in the mechanical properties.

### 4.2.2 Thermal properties

The thermal properties of lime sludge-HDPE composites are studied using DSC and TG analysis in order to assess the thermal behaviour and stability of the composites at higher temperatures in comparison to pure HDPE. Analysis of three composites (10 LS HDPE, 20 LS HDPE, and 30 LS HDPE) along with pure HDPE is discussed in the following sections.



(a) Heating cycle.



(b) Cooling cycle.

**Figure 4.14:** DSC thermogram during heating and cooling cycles for lime sludge-HDPE composites and pure HDPE.

#### 4.2.2.1 DSC Analysis

DSC measurements are conducted in order to determine the thermal properties such as melting temperature ($\mathrm{T_m}$), onset melting temperature ($\mathrm{T_{on}}$), heat of fusion ($\mathrm{H_m}$), heat of crystallization ($\mathrm{H_c}$), degree of crystallinity ($\chi_\mathrm{c}$), onset crystallization temperature ($\mathrm{T_{con}}$), and peak crystallization temperature ($\mathrm{T_c}$). Comparative studies on DSC thermograms of pure HDPE, 10 LS HDPE, 20 LS HDPE and 30 LS HDPE composites are carried out. From the recorded heating and cooling curves for these composites as shown in Figs. 4.14(a) and 4.14(b) respectively, the thermal properties are calculated and tabulated as shown in Table 4.2. The percentage of crystallinity ($\chi_\mathrm{c}$) in pure HDPE and its composites are calculated based on the formula provided by Liu et al. [150] as shown in Eq. (4.1).

$$\chi_\mathrm{c} = \frac{\mathrm{H_m}}{\mathrm{H_m^o w}} \times 100 \tag{4.1}$$

where $\mathrm{H}_\mathrm{m}^{o}$ is the heat of fusion for 100% crystalline HDPE, i.e., 293 J/g [253] and w is the mass fraction of HDPE in the composites.

It is observed that there is a slight increment in the melting temperatures and the onset melting temperatures of the composites with the addition of the lime sludge filler in the composites. The onset melting temperature increased from 121.72 °C to 123.88 °C and the melting temperature increased from 126.83 °C to 132.17 °C with the addition of filler. The melting enthalpy decreased with the increasing filler content indicating that the required heat to melt the polymeric composite decreased. This translates into money and power savings during extrusion and molding of polymeric composite fabrication [71]. Calculation of the percentage crystallinity of pure HDPE and each of the composites (10%, 20% and 30% filled lime sludge) reveals that percentage crystallinity decreased (from 77.66% for virgin polymer to 56.93% for 10 LS HDPE) with the addition of increasing filler loading. It is evident that in the present case, lime sludge particles reduce the conformational changes available to the polymer macromolecules during crystallization. $\mathrm{CaCO_3}$ present in lime sludge restricts the macromolecular ability thereby, reducing the spaces available for the polymeric macromolecules to arrange themselves according to statistical thermodynamics [71, 247]. This means that addition of lime sludge retards crystal growth in composites, thus reducing crystallinity. However, it is also a well known fact that one of the significant effects of particulate fillers on the crystallinity of semi-crystalline polymers is their capability to act as nucleating agents [55, 141, 194]. In this case as well, it is observed that the percentage crystallinity improved (56.93%

for 10 LS HDPE to 62.14% for 30 LS HDPE) as lime sludge content increased in the composites. This indicates that lime sludge could also act as a nucleating agent, thus increasing the amount of crystallinity in the composites.

Lime sludge induced restriction in the movement of polymer chain segments and depletion of the free spaces available for the macromolecules to occupy them, retards crystal growth [54]. This reduction in the conformational changes can be attributed to the decrease in the entropy of crystallization ($\Delta S_c$) given in Eq. (4.2)

$$\Delta \mathrm{S_c} = \frac{\mathrm{H_c}}{\mathrm{T_c}} \tag{4.2}$$

where, $\mathrm{H_c}$ is the crystallization enthalpy and $\mathrm{T_c}$ is the peak crystallization temperature. As seen in Table 4.2, it is evident that $\Delta \mathrm{S_c}$ decreased with increasing lime sludge filler loading which may be attributed to the high content of $CaCO_3$ present in the lime sludge which reduces the free volume/freedom available to the macromolecules (retarding crystal growth) [53, 54, 218]. The decrease in crystallinity index also indicates lesser heat required for melting during extrusion and molding, thus contributing to power saving and financial benefits. Herein, values of $\Delta \mathrm{S_c}$ denote the reduction in the degree of freedom available for the movement of macromolecules contributing to crystal growth. From the thermal analysis, it is evident that there are two contrasting properties exhibited by the polymeric composites due to the addition of $CaCO_3$ rich lime sludge – (a) acting as nucleating agent and (b) crystal growth retarders [54]. In this case, it is evident that the effect of lime sludge initially as a crystal growth retarder far surpasses its ability to act as nucleating agent. Hence, a decrease in the degree of crystallinity with upon lime sludge addition is observed. However, as lime sludge content increases (from 10 to 30 wt %), it slightly increases the amount of crystallinity as it also acts as heterogenous nucleation sites in the composites.

**Table 4.2:** DSC results (heating and cooling) of pure HDPE and lime sludge - HDPE composites

| Sample | Heating | | | | Cooling | | | |
|---|---|---|---|---|---|---|---|---|
| | $\mathrm{T_{on}}$ (°C) | $\mathrm{T_m}$ (°C) | $\mathrm{H_m}$ (J/g) | $\chi_c$ (%) | $\mathrm{T_{con}}$ (°C) | $\mathrm{H_c}$ (J/g) | $\mathrm{T_c}$ (°C) | $\Delta S_c$ (J/g°C) |
| Pure HDPE | 121.72 | 126.83 | 228.10 | 77.66 | 115.51 | 205.93 | 112.10 | 1.84 |
| 10 LS HDPE | 120.92 | 131.40 | 150.43 | 56.93 | 116.95 | 151.30 | 114.75 | 1.32 |
| 20 LS HDPE | 121.08 | 130.04 | 144.14 | 61.37 | 117.61 | 133.60 | 114.98 | 1.16 |
| 30 LS HDPE | 123.88 | 132.17 | 127.70 | 62.14 | 117.70 | 121.80 | 115.32 | 1.05 |

#### 4.2.2.2 TGA analysis

Thermal parameters such as thermal degradation, onset temperature, temperature at the maximum rate of weight loss and % residual weight left at 600 °C are used in order to conduct comparative analysis of thermal decomposition between lime sludge-HDPE composites (10 LS HDPE, 20 LS HDPE, and 30 LS HDPE) and pure HDPE.

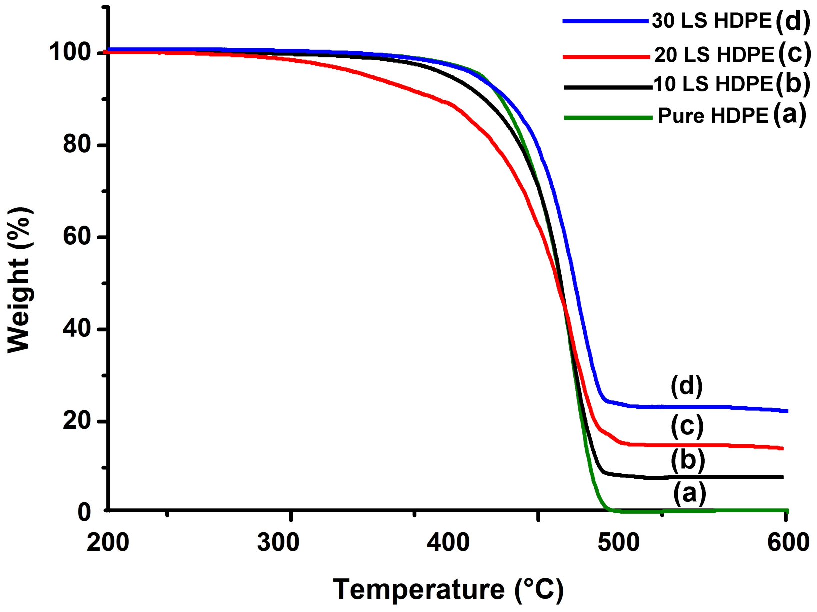
TGA analysis is conducted in order to study the thermal stability of lime sludge filled HDPE composites in comparison with pure HDPE. TGA (weight% *vs.* temperature) and DTG (Derivative of weight% vs temperature) thermograms are plotted as shown in Figs. 4.15(a) and 4.15(b) respectively. The results calculated from the thermograms for each composition of composites and pure HDPE are tabulated as shown in Table 4.3. From the thermograms, it is observed that the thermal stability improved with increasing lime sludge filler loading in the HDPE matrix. This is evident from the fact that the onset temperature for thermal degradation ($T_{on}$) increased from 429.38 °C for pure HDPE to 448.28 °C for 30% lime sludge filled HDPE composites. Additionally, the temperature at which maximum weight loss % ($T_{max}$) also increased with increasing lime sludge percentage in the composites indicating that the initial degradation product is the polymer, while further degradation in the composites are absorbed by the lime sludge, thus increasing the temperature of the point of maximum degradation. This is also confirmed by the amount of residual weight % of material left at 600 °C which increased from 0.69% for pure HDPE to 21.6% for 30 LS HDPE.

**Table 4.3:** TGA results of pure HDPE and lime sludge – HDPE composites

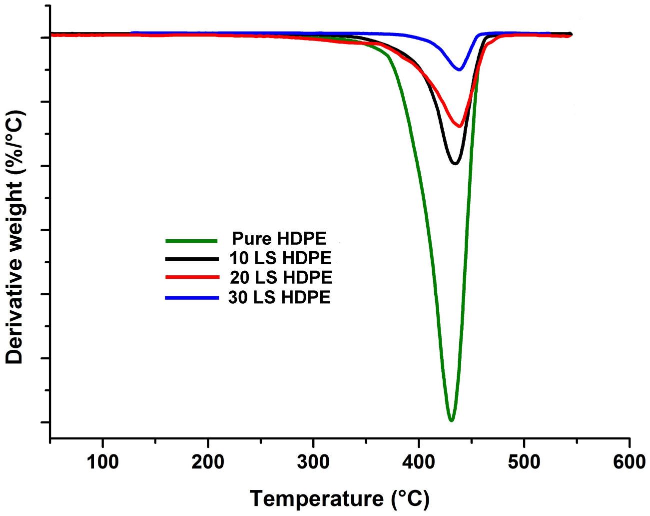
| Sample | Residual weight % | $T_{max}$ (°C) | $T_{on}$ (°C) |
|---|---|---|---|
| Pure HDPE | 0.69 | 468.27 | 429.38 |
| 10 LS HDPE | 7.75 | 468.92 | 430.91 |
| 20 LS HDPE | 14.5 | 471.90 | 434.94 |
| 30 LS HDPE | 21.6 | 476.33 | 448.28 |

## 4.3 Morphological Analysis of lime sludge-HDPE composites

Effective dispersion of the filler in a polymeric matrix and bonding at the fillermatrix interface are two prime factors varying the mechanical properties of polymeric composites. As observed from the micrograph of lime sludge particles in Fig. 4.1, the size of a lime sludge powder particle is less than or equal to 2 $\mu$m.



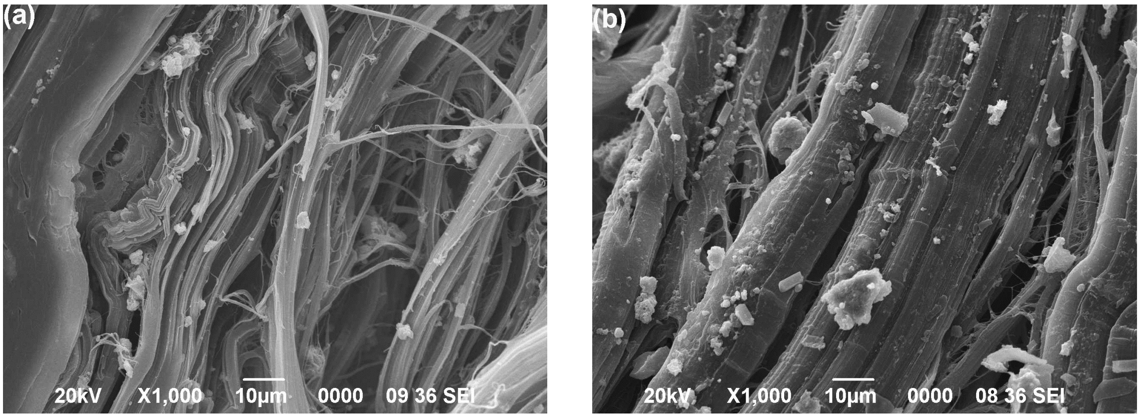
(a) TGA.



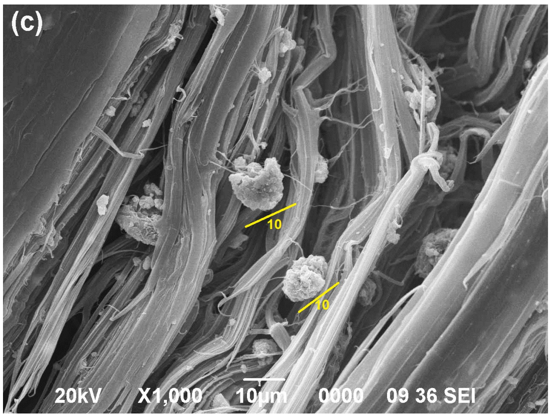
(b) DTG.

**Figure 4.15:** TGA and DTG plots for lime sludge – HDPE composites and pure HDPE.

Figures. 4.16(a), 4.16(b) and 4.16(c) shows the secondary electron micrographs of the three composites 10 LS HDPE, 20 LS HDPE, and 30 LS HDPE, respectively, obtained at the elongated fractured portion of the respective tensile test specimens. It is observed that with increasing amount of lime sludge in the composite, the tendency of the filler particles to agglomerate also increased. The particle dispersion and size are uniform in 10 LS HDPE and 20 LS HDPE composites when compared



(a) 10 LS HDPE. (b) 20 LS HDPE.



(c) 30 LS HDPE.

**Figure 4.16:** SEM micrographs at the fractured portion of the tensile test specimen for lime sludge-HDPE composites.

with 30 LS HDPE (Figure 4.16(c)) where particle agglomeration is observed. Figure 4.16(c) shows that for 30 wt % lime sludge-HDPE composite, the lime sludge particle size is approximately 10 $\mu$m which indicates agglomeration of particles. This is in conformation with the fact that the tensile strength decreased for 30 LS HDPE composite due to poor particle dispersion and higher filler particle size. This increased the stress concentrations at localized regions causing embrittlement of the composite. Dewetting due to debonding of the filler and matrix at the interface is clearly evident from the micrographs. It is also observed that lime sludge particles fell out of the matrix at isolated locations creating voids. This condition of poor adhesion between the filler and matrix is in correlation with the fact that the tensile strength of pure polymer was higher than that of the composites as debonding occurred due to the non-adherence of filler particles to the matrix. Thus, the filler particles are unable to handle the stress upon loading, leading to lower tensile strength observed in polymeric composites.

## 4.4 Water absorption properties

The water absorption (WA) behavior of the lime sludge filled HDPE composites determined by Eq. (3.6) is shown in Fig. 4.17. Generally, HDPE hardly absorbs water due to its hydrophobic structure; however, $CaCO_3$ rich lime sludge can absorb water because of its hydrophilic nature. It is observed that lime sludge particles increased the WA of the composites almost linearly in the initial stages, subsequent to which it reaches a saturation limit; and beyond which there is no more water uptake by the composites. The water uptake increased with increasing filler loading for the lime sludge filled composites with 30 wt % filler composite recording the highest water uptake. Additionally, the water uptake of 30 wt % filler composite is much higher suggesting that particle agglomeration and higher filler content created higher surface area for water absorption. The obtained results suggest that the WA of the composites depends on the parameters such as filler loading and filler particle size. Similar increase in the water absorption behaviour with increasing filler content was reported earlier by Rosa et al. [211] in case of rice husk filled polypropylene composites. Effect of WA on composites are important; as it is observed in earlier studies that in case of polymeric composites, as the amount of WA increases the mechanical properties such as tensile strength, flexural strength, flexural modulus and fracture toughness decreases due to the degradation caused in the composite structure due to more water uptake by the reinforcing filler or fibres [13, 127, 268]. Thus, WA lowers the mechanical properties of polymeric composites as a result of moisture absorption.

## 4.5 Regression analysis

It is imperative to state that in order to use lime sludge as filler in HDPE composites commercially, weight fraction of lime sludge to be added as filler must be correctly predicted in order to obtain the desired mechanical properties in the composites. Hence, different mechanical properties as a function of weight fraction of lime sludge filler are modelled using non-linear regression analysis. Fourth-order regression equations are developed for all mechanical properties (tensile strength, tensile modulus, elongation at break, flexure strength, flexure modulus, and impact strength) using the observed experimental data. The regression equations developed provided excellent fit for the variations of all mechanical properties as a function of lime sludge filler in composites. The regression equations from Eq. (4.3) to Eq. (4.8)

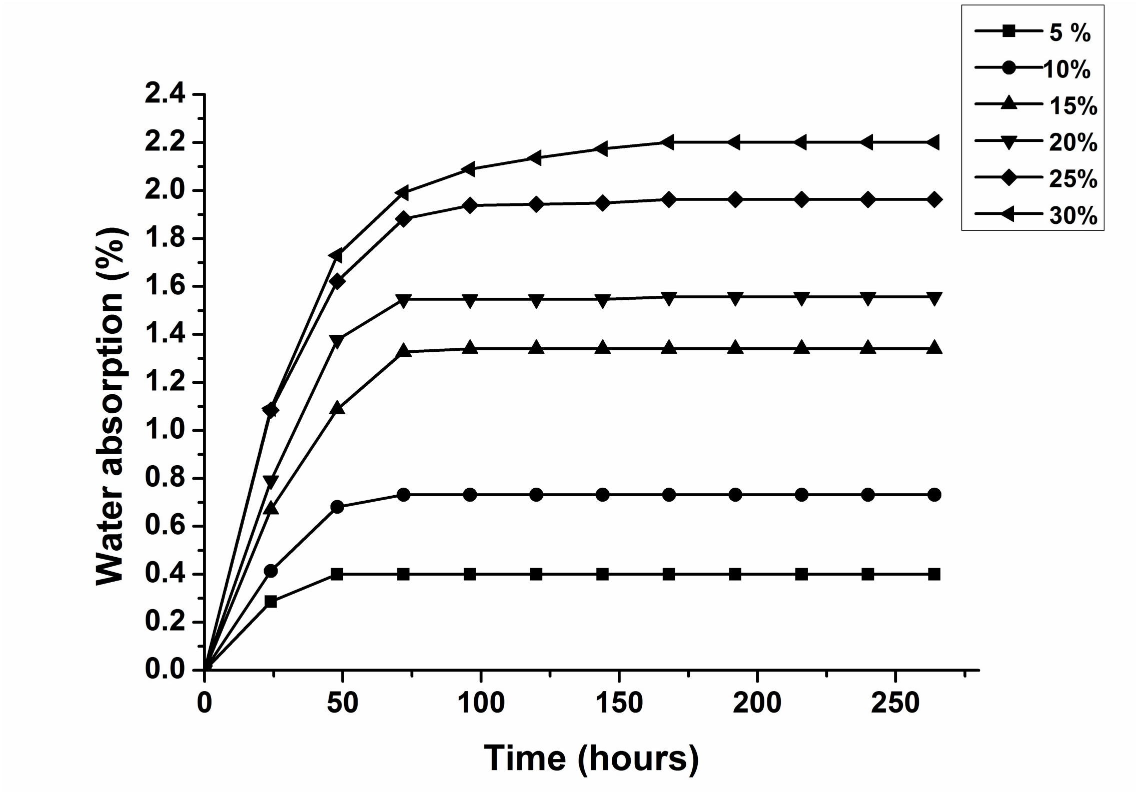


**Figure 4.17:** Water absorption *vs.* time for various lime sludge filler loading in HDPE composites.

are provided below:

$$\mathrm{TS} = -197839\mathrm{x}^5 + 159661\mathrm{x}^4 - 46129\mathrm{x}^3 + 5692.5\mathrm{x}^2 - 283.76\mathrm{x} + 16.861; R^2 = 0.9747 \tag{4.3}$$

$$\mathrm{TM} = 44921\mathrm{x}^4 - 24691\mathrm{x}^3 + 4659.3\mathrm{x}^2 - 133.4\mathrm{x} + 139.01; R^2 = 0.9979 \tag{4.4}$$

$$\mathrm{EB} = -863930\mathrm{x}^4 + 621011\mathrm{x}^3 - 133026\mathrm{x}^2 + 4859.5\mathrm{x} + 786.45; R^2 = 0.9423 \tag{4.5}$$

$$\mathrm{FS} = 292.42\mathrm{x}^4 + 276.21\mathrm{x}^3 - 199.83\mathrm{x}^2 + 46.644\mathrm{x} + 6.3048; R^2 = 0.9818 \tag{4.6}$$

$$\mathrm{FM} = -286788\mathrm{x}^4 + 204662\mathrm{x}^3 - 51071\mathrm{x}^2 + 5920.4\mathrm{x} + 248.81; R^2 = 0.9902 \tag{4.7}$$

$$\mathrm{IS} = 36349\mathrm{x}^4 - 26531\mathrm{x}^3 + 6683.8\mathrm{x}^2 - 673.5\mathrm{x} + 29.972;\ R^2 = 0.99 \tag{4.8}$$

Thus, Fig. 4.18 shows the consolidated image of the curves derived from Eq. (4.3) to Eq. (4.8). The Y-axis has been normalized so that all the mechanical properties lie in the range of 01. Using Fig. 4.18, based on the desired mechanical properties, a user will be able to determine the weight fraction of raw lime sludge required in HDPE composite, e.g. if a user requires HDPE composites having tensile modulus of  140 MPa and strength in the range of 11-12 MPa, then based on Fig. 4.18, a 5 wt % lime sludge may be chosen as the filler in the HDPE matrix which would provide the required mechanical properties. However, other mechanical properties such as elongation at break of 680 %, flexural strength of 8.4 MPa, flexural modulus of 452.7 MPa, and impact strength of 8.9 J/m for a 5 wt % filler composites must be considered beforehand (using Fig. 4.18), in order to ensure whether they satisfy the acceptable limits criteria for these parameters. This is depicted in the Fig. 4.19.

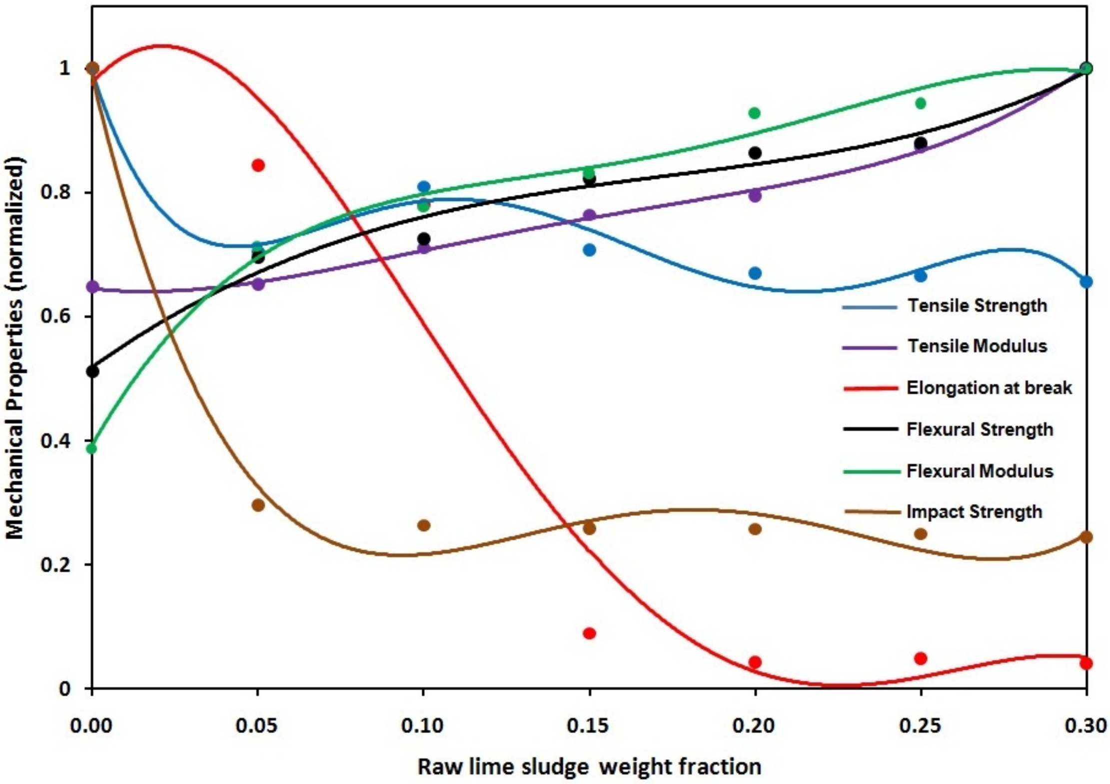


**Figure 4.18:** Normalized plot of mechanical properties as a function of lime sludge filler wt % obtained through regression analysis.

## 4.6 Summary

Industrial lime sludge waste is usually disposed in dumpyards causing pollution. Hence, the feasibility of using lime sludge waste as a filler in polymeric composites is discussed in this chapter. For this purpose, the lime sludge-HDPE composites are fabricated with varying weight fraction of lime sludge filler in an HDPE matrix. Subsequently, the mechanical, thermal and morphological properties of these composites are characterized. The summary of the chapter is as follows:

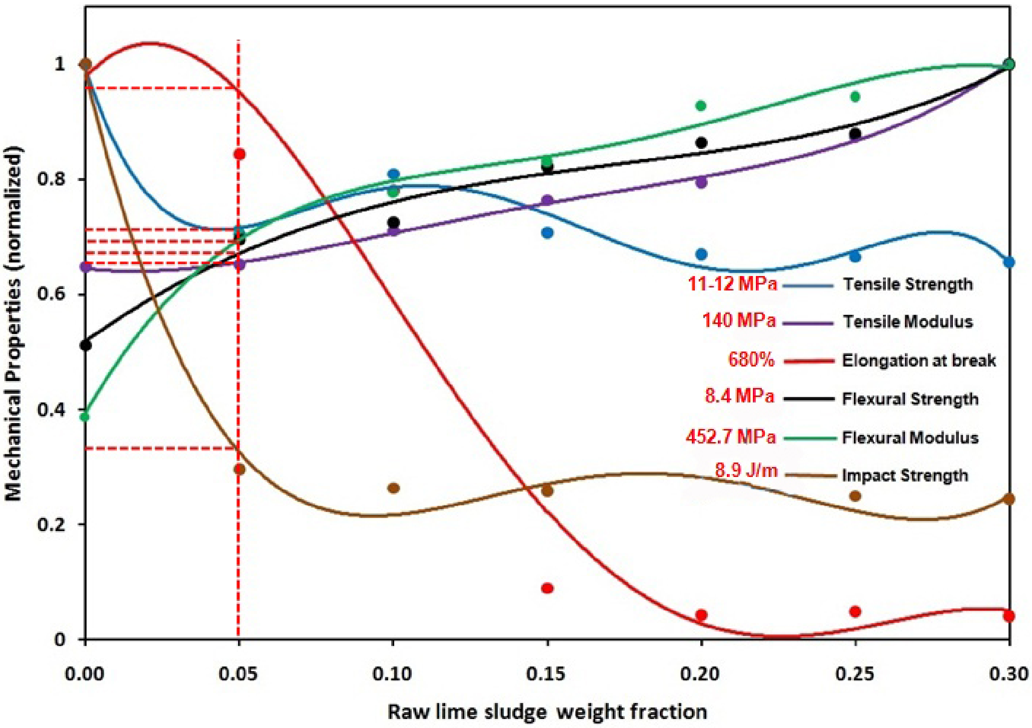


**Figure 4.19:** Normalized plot of mechanical properties depicting the use of the regression based model.

- The tensile strength decreased when compared with virgin HDPE (tensile strength of 16.88 MPa), upon addition of lime sludge to the composites. However among the composites, the tensile strength increased up to 10 wt % of lime sludge (from 11.91 MPa for 5 wt % to 13.67 MPa for 10 wt %) suggesting effective reinforcement; beyond this it started to decrease again (11.09 MPa for 30 wt %). Morphological analysis revealed that particle agglomeration at higher filler loading and low interfacial adhesion at the filler-matrix boundary is responsible for the low tensile strength. The flexural strength also increased with increasing filler loading (from 6.23 MPa for pure polymer to 12.19 MPa for 30 wt %) as lime sludge acts as a better reinforcement under bending stresses due to effective stress transfer between the matrix and filler particles under bending stresses.

- The tensile and flexural modulus increased by 54% (139.25 MPa for pure polymer to 215.2 MPa for 30 wt%) and 158% (245.7 MPa for pure polymer to 635 MPa for 30 wt%) respectively upon the addition of rigid lime sludge particles due to the introduction of a mechanical restraint causing restriction in deformation within the elastic limit.

- Particle agglomeration at higher filler loading (high stress concentration sites) and low interfacial adhesion are also responsible for the decrease in the ductility (elongation at break decreased from 806% for pure polymer to 32.8% for 30 wt%) and impact strength (30.2 J/m for pure polymer to 7.35 J/m for 30 wt%) of the composites.

- DSC analysis revealed that the onset melting (121.72 °C for pure polymer to 123.88 °C for 30 LS HDPE) and melting temperatures (126.83 °C for pure polymer to 132.17 °C for 30 LS HDPE) increased while the melting enthalpy decreased from 228.10 J/g to 127.70 J/g (*i.e.* less heat required to melt the composites), upon lime sludge addition in HDPE composites. Decrease in the degree of crystallinity with lime sludge addition shows that it acts as a crystal growth retarder; thus reducing the conformational changes available to the polymer macromolecules during crystallization. However, lime sludge also acts as heterogenous nucleating sites, which slightly increases the amount of crystallinity as its content increases in the composites (*i.e.* 10 wt % to 30 wt %).

- TGA analysis revealed that lime sludge filler improved the thermal stability of the composites by increasing the onset temperature for thermal degradation (429.38 °C for pure polymer to 448.28 °C for 30 LS HDPE), temperature at which maximum weight loss occurs (from 468.27 °C to 476.33 °C) and residual weight % left at 600 °C (from 0.69% to 21.6% residual weight).

- The water absorption rate increased with increasing filler loading (from 0.404% for 5 wt % lime sludge filled composites to 2.2% for 30 wt % lime sludge filled composites). This suggests that particle agglomeration and higher filler content created higher surface area for water absorption at higher filler loadings in the composites.

- Non-linear regression equations are developed for each mechanical property as a function of lime sludge loading. A consolidated model was constructed with the normalized data for all the mechanical properties. This model would simultaneously predict the values of mechanical properties with varying lime sludge content.