Chapter 5

Stearic acid coated lime sludge filled HDPE composites

When fatty acids are adsorbed onto carbonate surface, a monolayer of hydrophobic organic molecules is attached to the mineral surface. This ultrathin organic film strongly influences the final properties of the composites, as it is the interface which determines the particle-particle as well as the particle-matrix interactions. Fatty acids such as stearic acid help in uniform dispersion of particles in the polymeric matrix as the tendency of the coated filler particles to agglomerate reduces substantially. Additionally, stearic acid is cheaper and more widely available than its contemporary surface modifiers such as silanes, maleic anhydride, titanates, etc. Needless to say, for lime sludge to be an attractive option in terms of its commercial viability, it has to be inexpensive in terms of its availability and for composite processing. In this context, stearic acid proves to be a potentially effective option as a surface modifier of lime sludge. This study explores the feasibility of using stearic acid coated lime sludge as a reinforcing filler in HDPE composites. Thus, this chapter illustrates the mechanical, thermal, morphological, and water absorption properties of stearic acid coated lime sludge reinforced HDPE composites, with a view to highlight the advantages of using stearic acid as a surface modifier on lime sludge while using it as a filler in polymeric composites. 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.

5.1 Stearic acid coating on lime sludge - FTIR spectroscopy

Fig. 5.1 shows FTIR spectra of pure HDPE, lime sludge, and stearic acid coated lime sludge-HDPE composites (10 LS SC, 20 LS SC, and 30 LS SC) respectively. The wave numbers 2959 and 2669 cm^{-1} can be attributed to the functional group C-CH_3 while 2853 cm^{-1} can be attributed to CH_2 functional group of HDPE [225]. Additionally, typical IR bands of HDPE appear at 2925, 1377, and 1464 cm^{-1} (CH_3 functional group with C-H bending), 1360 cm^{-1} (-CO-CH_3 functional group with -CH_2 symmetric vibration in ether), 909 and 993 cm^{-1} (-CH=CH_2 with C-CH_2 out of plane bending), and 718 and 676 cm^{-1} (-CH=CH-*cis* functional group) [69, 88, 225, 226]. The lime sludge spectrum shows IR peaks at 876, 1455 (broad spectrum), and 714 cm^{-1} corresponding to $v2-$ symmetric bending, $v3-$ asymmetric stretching and $v3-$ asymmetric bending vibrations, which are characteristic of the calcite structure of calcium carbonate present in lime sludge [68]. However, in the FTIR spectra of composites, it is observed that only two peaks at 716 and 879 cm^{-1} can be assigned to the $CaCO_3$ structure present in the composite. Additionally, the peaks at 1793, 2516, and 2873 cm^{-1} can also be attributed to the presence of calcite (doubly degenerate asymmetric stretching, CO_3 stretching, C=O stretching) [134]. The presence of stearic acid in the composites can be attributed to the presence of the absorption bands at 2850 and 2919 cm^{-1} corresponding to the symmetric stretching vibration peak of -CH_2 group and asymmetric stretching vibration peak of -CH_2 group [151].

5.2 Mechanical and morphological 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.

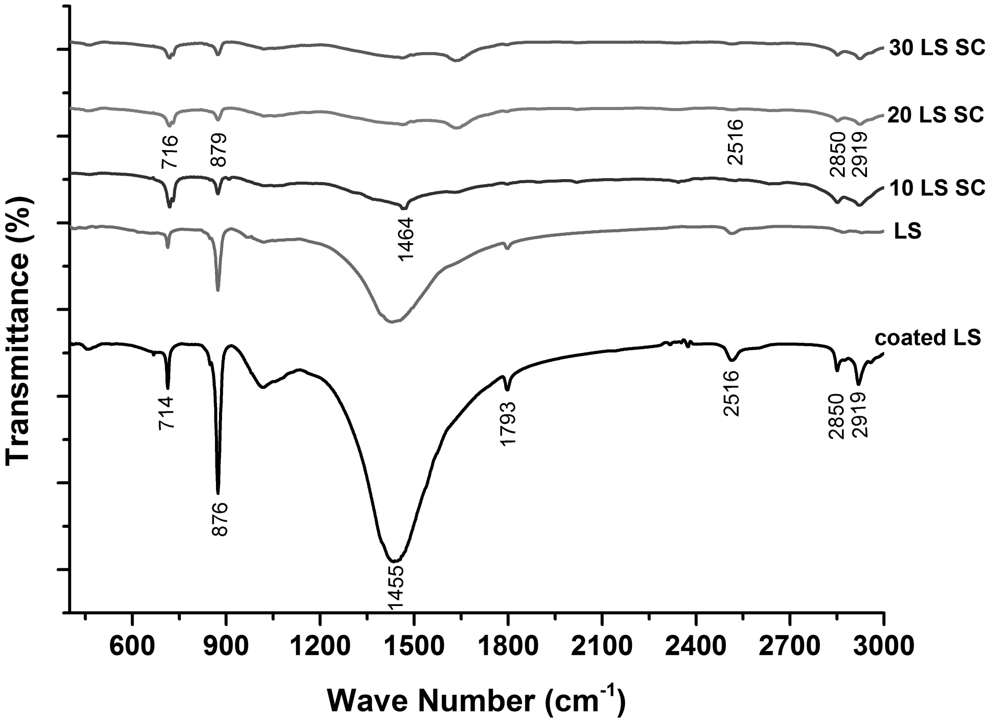


Figure 5.1: FTIR spectrum for raw lime sludge, stearic acid coated lime sludge and stearic acid coated lime sludge-HDPE composites.

5.2.1 Tensile strength

The sample stress-strain curves for HDPE and raw lime sludge filled HDPE with increasing weight fraction of lime sludge loading derived after tensile testing is shown in Fig. 5.2. The variation in tensile strength with increasing uncoated and coated filler loading is shown in Fig. 5.3(a). It is found that there is a moderate drop in the overall tensile strength with increasing filler loading for both uncoated and stearic acid coated lime sludge when compared with pure HDPE. This is attributed to low bonding between the filler particles and the matrix, leading to filler-matrix interfacial dewetting under tensile loading. This trend is in agreement with the findings of the previous researches on particulate composites [20, 222]. However, two distinct observations are made when tensile strength data of the uncoated and coated filler composites are compared (1) the tensile strengths of the stearic acid coated lime sludge composites are higher than that of the uncoated filler composites for all filler wt %; (2) the individual peak tensile strengths are observed at 10 wt % for uncoated (13.67 MPa) and at 25 wt % loading for coated (15.08 MPa) filler composites, respectively. Higher tensile strengths of coated filler composites as compared to uncoated composites indicate better physical interaction and entanglement between the long hydrophobic chains of stearic acid moiety present on the lime sludge particles and the hydrophobic HDPE chains. Additionally, stearic acid coating makes the lime sludge particles hydrophobic in nature; thus, hindering agglomeration (refer Fig. 5.3(c)) and increasing their dispersion in the HDPE matrix [158]. This is evident from the SEM micrograph of the uncoated composite at 25 wt % filler loading shown in Fig. 5.3(c). The fractured surface of the uncoated composites shows presence of voids (due to particle debonding and fall out) and partially brittle fracture surface. However, it has been revealed earlier that the lime sludge consists irregular shaped particulate structures with an average diameter of approximately 2 μm (refer Fig. 5.3(b)). The voids present in Fig. 5.3(c) are much bigger in size suggesting particle agglomeration. However, in case of coated composites, the particle distribution is uniform with lesser void and no particle agglomeration in case of coated filler composites. Hence, the peak tensile strength of coated lime sludge composites is observed at higher (25 wt %) filler loading as compared to uncoated lime sludge composites (10 wt %). The line diagram depicting the consequence of adding stearic acid coated lime sludge particles to the HDPE matrix (uniform dispersion) as compared to that of raw lime sludge filled composites is shown in Fig. 5.4.

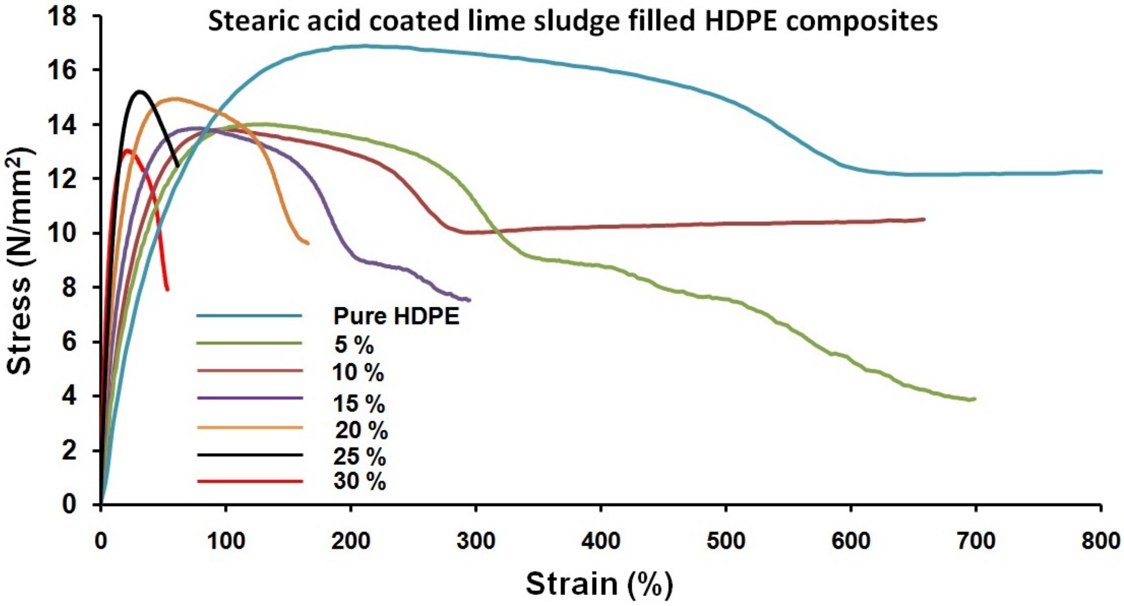
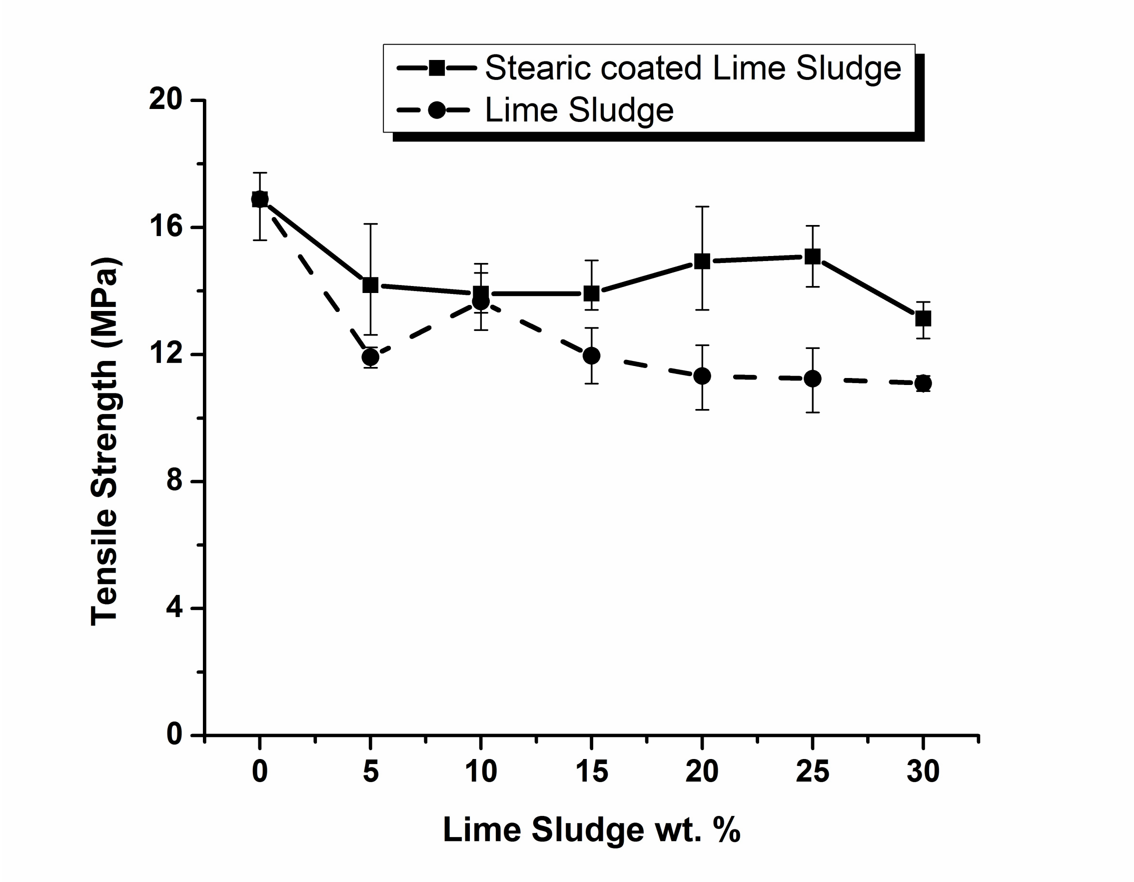


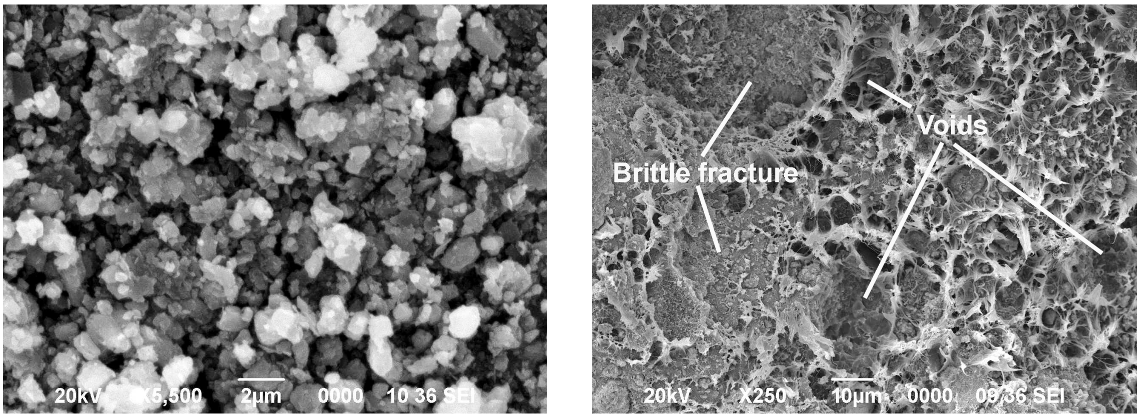
Figure 5.2: Sample stress-strain curves for HDPE and stearic acid coated lime sludge filled HDPE composites derived after tensile testing.

5.2.1.1 Morphological characterization

Fig. 5.5(a)-(f) shows the morphology at the elongated fractured surfaces of both uncoated and coated tensile test specimens at different filler loadings. From the Fig. 5.5(a)-(c) two details are evident (1) presence of voids due to debonding at



(a) Tensile strength vs. lime sludge wt %.



(b) Particle size.

(c) Fracture surface.

Figure 5.3: (a) Variation of tensile strength with increasing filler loading; SEM micrographs depicting (b) the particle size of lime sludge and (c) the fractured surface of lime sludge composite at 25 wt % filler loading.

the filler-matrix interface which increases as the filler loading is increased (specially in case of uncoated filler); and (2) particle agglomeration (larger particle size) at higher filler loading (25 wt %) in case of uncoated filler. This is in conformation with the fact that the tensile strength decreased at higher filler loading in case of

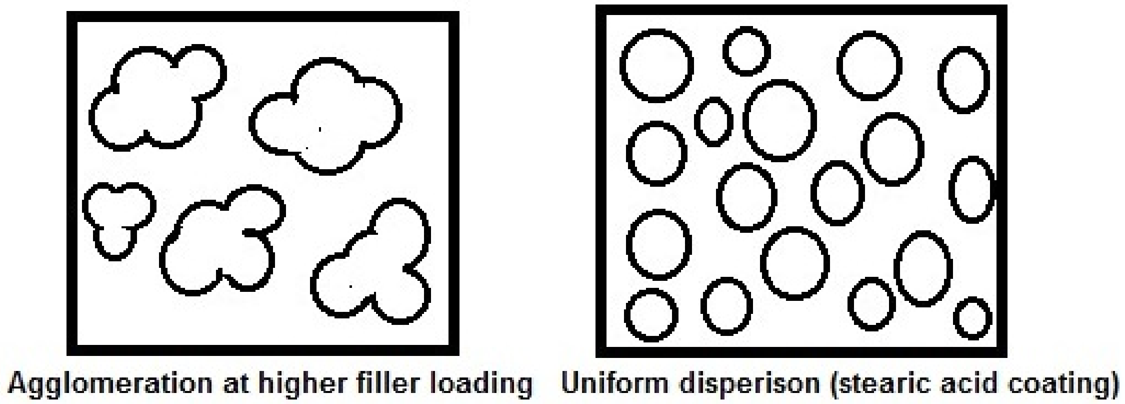

Agglomeration at higher filler loading
Uniform disperison (stearic acid coating)

Figure 5.4: Line diagram depicting coated lime sludge particles matrix (uniform dispersion) as compared to uncoated particulate composite (agglomeration).

uncoated composite. Poor particle dispersion and higher filler particle size (stress concentrations at localized regions) caused embrittlement of the uncoated composite.

However, particle dispersion in coated composites is uniform up to 25 wt % filler loading and hence, they exhibit better strength than uncoated lime sludge filled HDPE composites (refer Fig. 5.5(d)-(f)) . Thus, stearic acid proves to be an efficient surface modifier for lime sludge particles and higher wt % of coated filler (25 wt %) can be used to fabricate composites with better tensile strength than uncoated filler composites (10 wt %). This means reduction in composite costs (more profit) and more utilization of the industrial waste. Furthermore, poor adhesion at the filler-matrix interface due to debonding and void creation is the reason for higher tensile strength of pure polymer than both coated and uncoated composites. However, peak tensile strengths at 10 wt % for uncoated and 25 wt % for uncoated lime sludge composites suggest that lime sludge acts as an effective reinforcement (better particle dispersion and filler-matrix bonding) up to their respective filler loading.

5.2.2 Tensile modulus

A significant increment in the tensile modulus of composites with increasing filler content (139.25 MPa for pure polymer to 193.75 MPa for 30 wt%) for stearic acid coated lime sludge filled composites is observed when compared with pure HDPE as shown in Fig. 5.6. The rise in the elastic modulus is largely attributed to: (1) replacement of a polymeric matrix with rigid particulate fillers; and (2) restriction in the chain mobility hindering deformation provided by the rigid lime sludge particles. This increase in the tensile modulus upon addition of rigid particulate fillers has also been reported in earlier studies [66, 149, 246]. However, the elastic modulus of stearic acid coated lime sludge composites are observed to be slightly lower than its

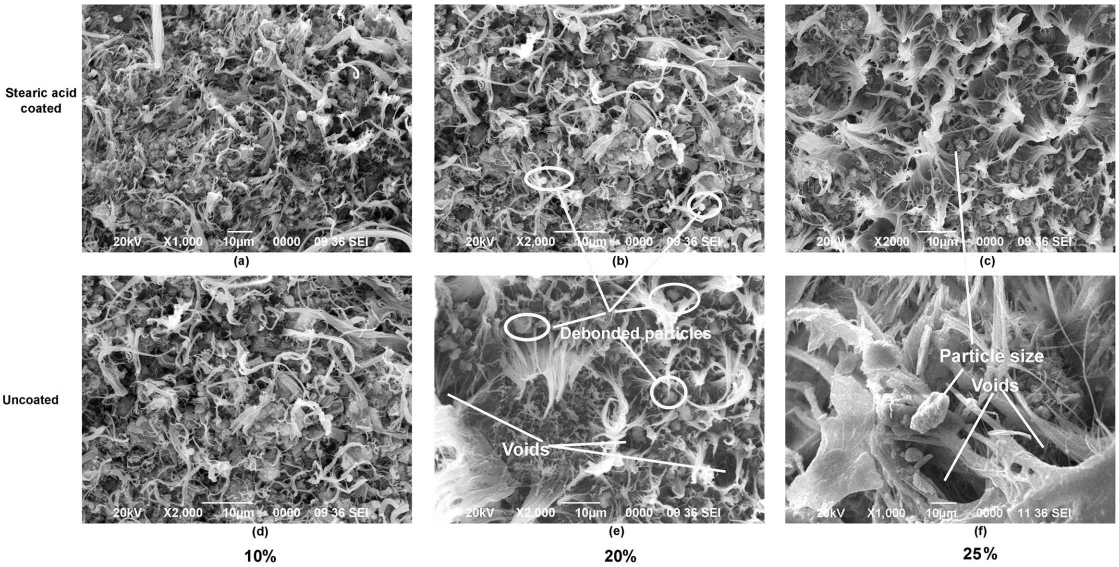


Figure 5.5: SEM micrographs of uncoated ((a)-(c)) and stearic acid coated ((d)-(f)) lime sludge filled HDPE composites at 10, 20, and 25 wt % filler loading.

uncoated counterpart indicating that the mechanical restriction to chain mobility is more pronounced in case of uncoated lime sludge composites. Similar trend in the decrease of tensile modulus upon stearic acid coating was reported by Zuiderduin et al. [286] in a previous study.

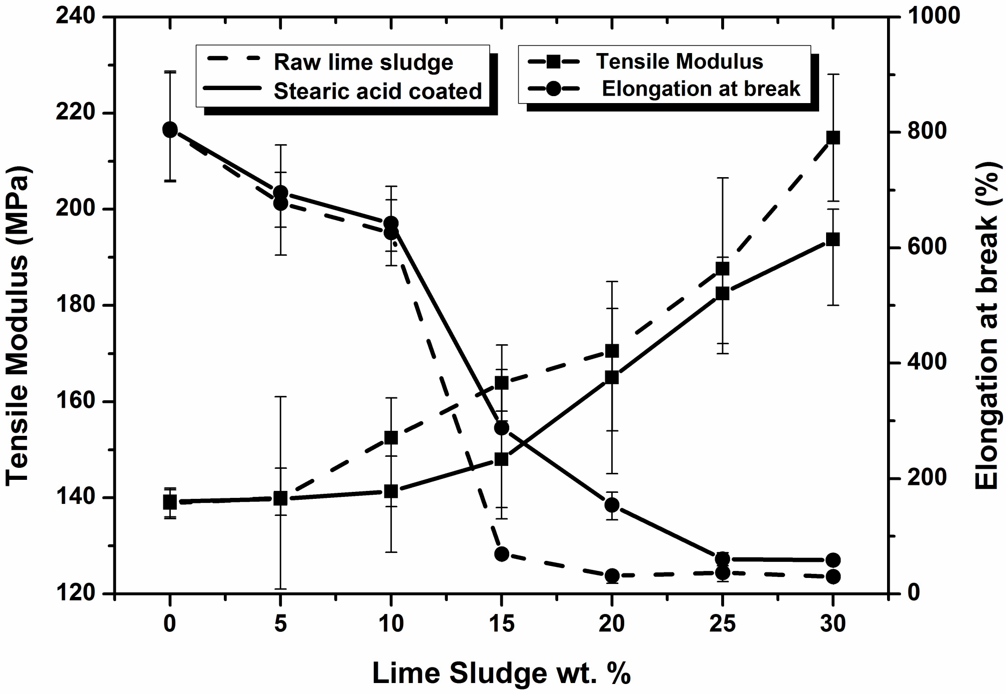


Figure 5.6: Variation of tensile modulus and elongation at break with increasing filler loading.

5.2.3 Elongation at break

As shown in Fig. 5.6, the elongation at break decreased drastically with increasing filler content a specific characteristic of particulate reinforced composites. Low elongation of rigid filler particles (restricts the flow of polymer molecules past one another), filler agglomeration at higher lime sludge concentration (stress concentration sites), and dewetting along filler-matrix boundary (ineffective stress transfer from the matrix to the filler particles) are prime reasons for the decrease in the ductility of the composites. However, the elongation at break values for coated composites (806% for pure polymer to 58.4% for 30 wt%) are observed to be higher than the uncoated ones at higher filler loadings (>10 wt %). As the effect of particle agglomeration on ductility is less prominent in stearic acid coated composites, hence, the ductility of coated composites is higher than its uncoated counterparts. Such increase in elongation at break and decrease in elastic modulus for stearic acid coated composites were also obtained by Rungruang et al. [215].

5.2.4 Flexural strength

The sample stress-strain curves for pure HDPE and HDPE composites with increasing weight fraction of coated lime sludge loading derived after flexural testing is shown in Fig. 5.7. Flexural strength increased (6.2 MPa for pure polymer to 12.5 MPa for 30 wt%) with increasing filler loading upon addition of coated particulate composites as shown in Fig. 5.8. Excess polymer on the surface as a result of the restriction imposed by the mold walls during molding of the composites led to smooth composite surfaces which hinder generation of cracks at the surface of the specimen (at top and bottom surfaces) during bending. 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 better stress transfer at the filler-matrix interface under bending stresses [124, 131, 141]. However, the flexural strength of stearic acid coated composites is observed to be higher than uncoated composites. The stearic acid coating provides two contradictory facts - (1) lowering of mechanical anchorage due to smoothening of lime sludge particles; and (2) better physical interaction and entanglement between the long hydrophobic chains of the stearic acid moiety present on the lime sludge particles and the hydrophobic HDPE chains under bending stresses. In this case, the second fact proved to be more prominent resulting in better flexural strength for stearic acid coated composites.

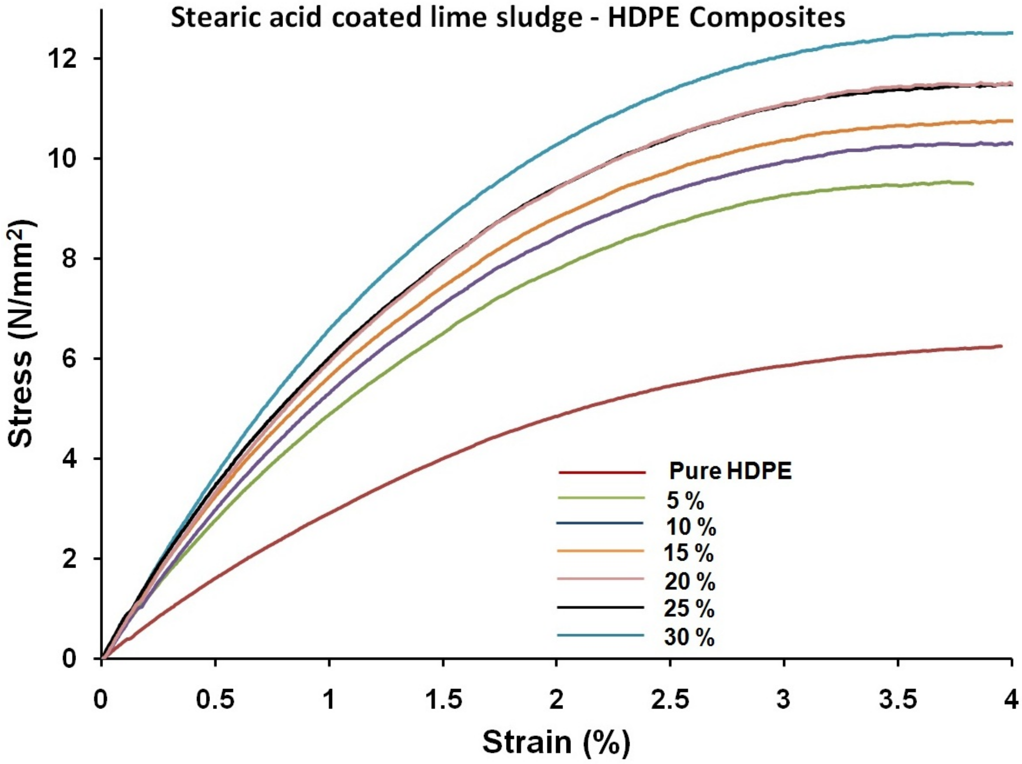


Figure 5.7: Sample stress-strain curves for HDPE and stearic acid coated lime sludge filled HDPE composites derived after flexural testing.

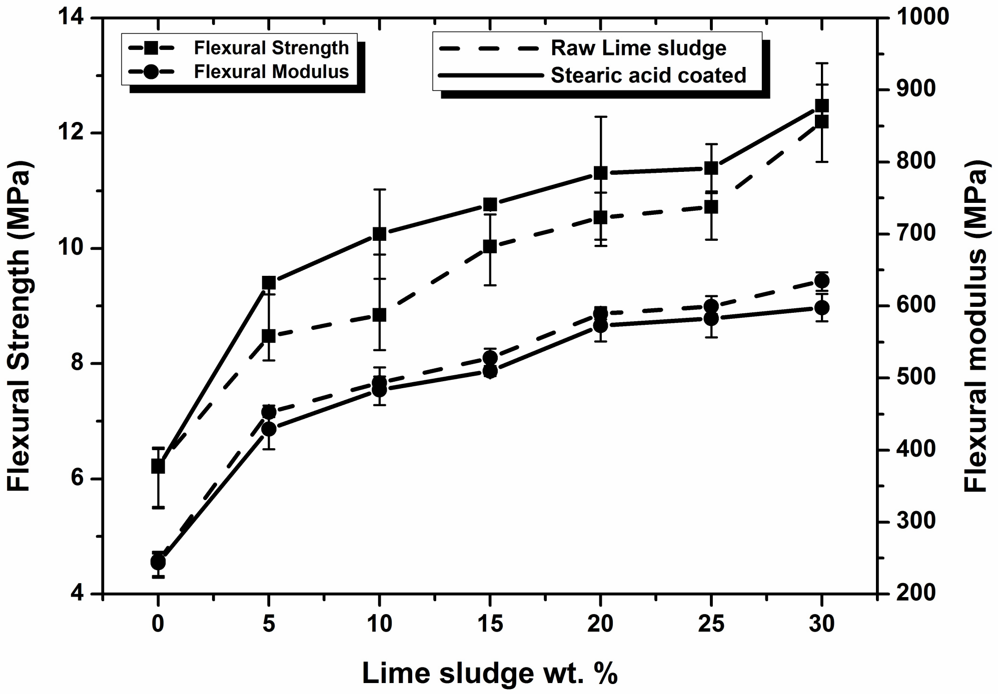


Figure 5.8: Variation of flexural strength and modulus with increasing filler loading.

5.2.5 Flexural modulus

Additionally in Fig. 5.8 it is shown that incorporation of rigid particulate filler improved the stiffness (flexural modulus) (245.7 MPa for pure polymer to 193.75 MPa for 600 wt%) of the coated lime sludge filled polymeric composites under bending stresses. Higher concentration of rigid particulate materials demands higher stress for the same amount of deformation and hence the increase in the flexural modulus. The increase in flexural modulus and strength with increasing filler loading was also obtained from previous studies [124, 131, 141]. Moreover, the mechanical restriction in chain mobility was found to be more pronounced (enhancement of filler rigidity) for uncoated lime sludge filled composites than for coated composites. The results obtained in this research seems to conform well with the tensile modulus values obtained in this study.

5.2.6 Impact strength

Impact strength of a composite depends on parameters such as toughness properties of reinforcement, nature of filler-matrix interface, and nature of fracture of the matrix [48]. It is observed that the impact properties decreased (30.2 J/m for pure polymer to 18.8 J/m for 30 wt%) with the introduction of filler materials for coated lime sludge filled composites when compared to pure HDPE (refer Fig. 5.9). Highly stiff composites in this case, exhibit low impact resistance because high stress is transferred from the polymeric matrix to the filler particles instantly. This decrease in the impact strength was also reported earlier in case of mineral particles filled polymeric composites [7, 208]. The lime sludge particles act as stress concentration sites which restrict plastic deformation. Upon impact, the crack propagates to the interfacial regions and the material fails in a brittle manner. However, the impact properties of stearic acid coated lime sludge composites are observed to be much higher than its uncoated counterpart. Stearic acid hinders particle agglomeration; hence the effect of large stress concentration sites on the impact properties is drastically reduced unlike that in uncoated composites.

5.3 Thermal Properties - TG analysis

Thermal parameters such as thermal degradation and percentage residual weight left at 600 °C are used in order to conduct comparative analysis of thermal decomposition between stearic acid coated and uncoated lime sludge-HDPE composites. TGA

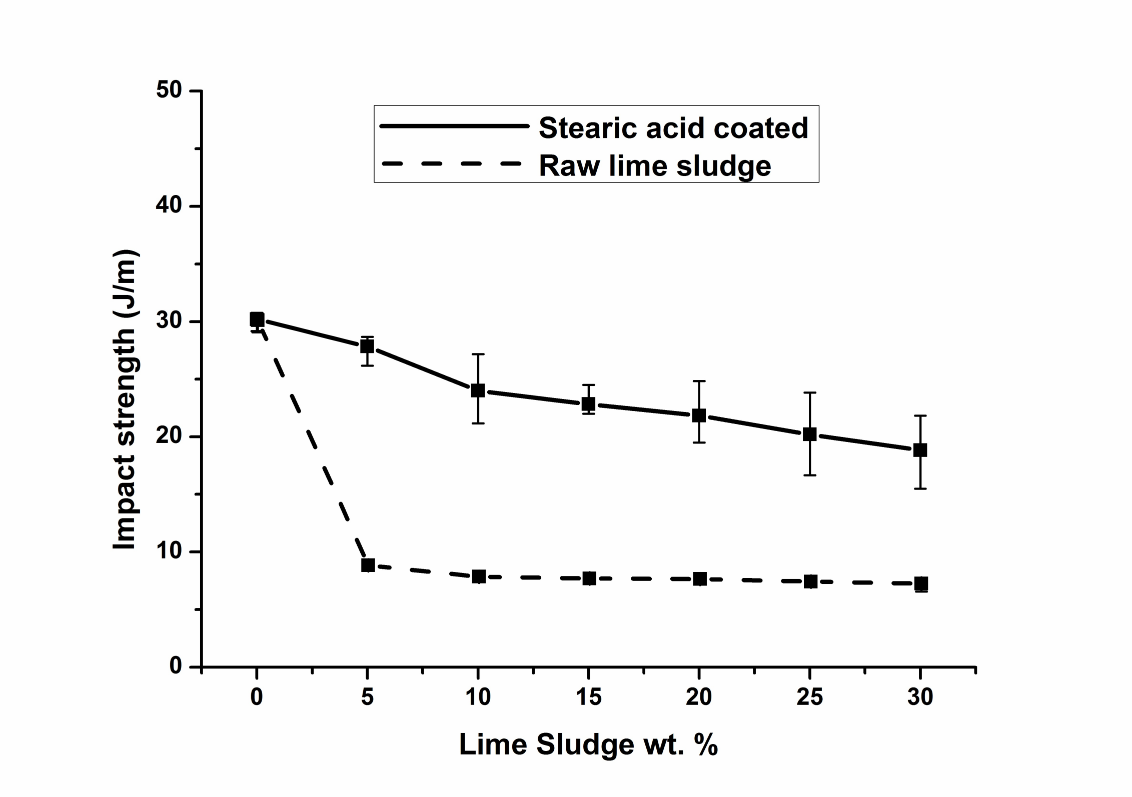


Figure 5.9: Variation of Izod impact strength with increasing filler loading.

curves are plotted for pure HDPE, uncoated, and coated filler (10, 20, and 30 wt %) composites. The results calculated from the TGA and DTG thermograms shown in Fig. 5.10(a) and Fig. 5.10(b), respectively, are tabulated in Table 5.1.

Table 5.1: Comparative TGA results of stearic acid coated and uncoated lime sludge filled HDPE composites.

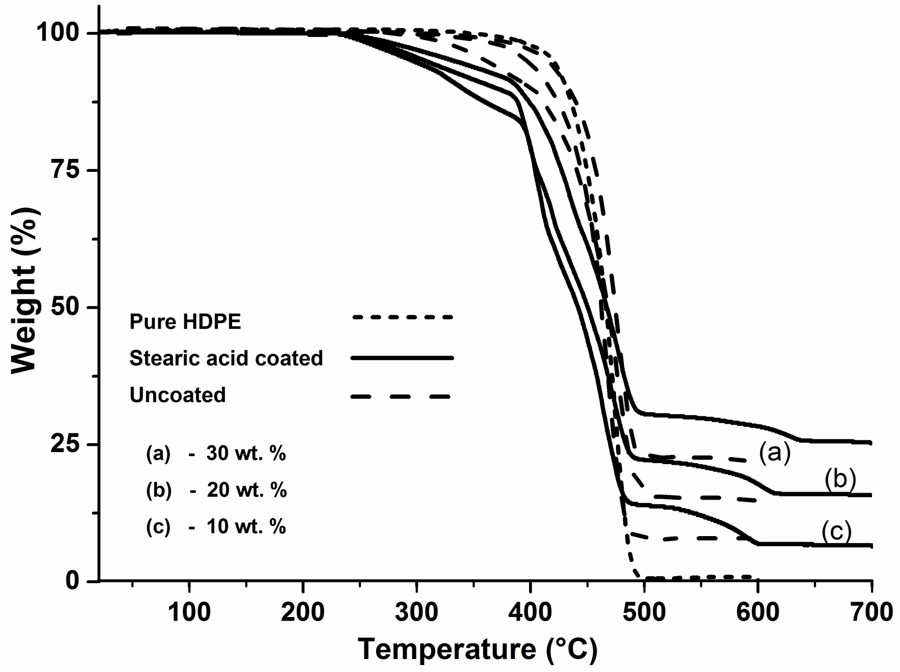
Sample	Residual weight at 500 °C (%)	Residual weight at 500 °C (%)	T_{max} (°C)
Pure HDPE	0.69	0.69	468.27
10 LS HDPE	7.75	7.75	468.92
10 LS SC	13.98	7.87	466.03
20 LS HDPE	14.5	14.50	471.90
20 LS SC	22.16	16.10	469.08
30 LS HDPE	21.6	21.60	476.33
30 LS SC	30.34	27.96	475.83

The temperatures at which maximum degradation (T_{max}) takes place show an increasing trend due to increasing filler loading. However, effect of surface modification is very insignificant in this case. It is observed from the thermograms that HDPE undergoes degradation at 429 °C while the onset degradation temperatures for uncoated filler composites range from 430 °C to 448 °C. On the contrary, in stearic acid coated lime sludge-filled composites, a light weight loss is observed between 250 °C and 400 °C which is associated with the degradation of stearic acid.

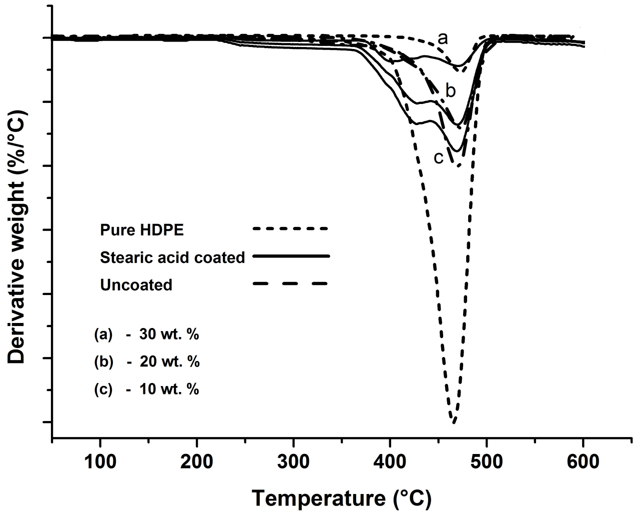
Subsequently, gradual decomposition of the HDPE matrix takes place in the range of 400 °C to 500 °C for uncoated composites when at 500 °C, $CaCO_3$ of lime sludge degrades to CaO leaving their respective residual weights. This connects well with the findings of previous researches [185, 199, 224]. While uncoated lime sludge composites decompose at 500 °C to their residual wt %; it is observed that the stearic acid coated filler composites decompose to their final residual wt % only above 600 °C (Fig. 5.10(a)). The weight loss from 500 °C to 600 °C may be attributed to the entanglement between the long hydrophobic chains of stearic acid moiety present on the lime sludge particles and the hydrophobic HDPE chains at the filler-matrix interface which increases the thermal stability of the composites in this range. This correlates well with the fact that the tensile and bending strengths of the coated filler composites are observed to be higher than the uncoated filler composites.

5.4 Water absorption properties

The water absorption (WA) behavior of stearic acid coated lime sludge filled HDPE composites determined by Eq. (3.6) is shown in Fig. 5.11. The obtained results suggest that the WA of the composites depends on the parameters such as filler loading and filler particle size. It is observed that lime sludge addition increased the WA of the polymeric composites almost linearly in the initial stages, subsequent to which it reaches a saturation limit beyond which there is no more water uptake by the composites. The water uptake increased with increasing filler loading (0.38% for 5 wt % for stearic acid coated lime sludge filled composites); with 30 wt % filler composite recording the highest water uptake of 1.8%. This influence of filler wt % on the water uptake is however, less dependent of the filler particle size. The influence of filler particle size is more pronounced when a comparison is made between the WA percentages of the coated and uncoated lime sludge composites at 30 wt %. The water uptake of 30 wt % uncoated filler composite (2.2%) is much higher than its coated counterpart (1.8%) suggesting that particle agglomeration and higher filler content at 30 wt % uncoated filler loading created higher surface area for WA. Stearic acid acts as a surfactant enhancing the wettability and dispersability of lime sludge particles in the HDPE matrix. This hinders the agglomeration tendency of lime sludge particles and decreases the space at the filler-matrix interface for water accumulation. This trend in the decreased water uptake upon stearic acid coating on wood flour particles was also observed in previous researches [60, 271]. Thus, stearic acid coating proved to be efficient in hindering the water absorption tendency of



(a) TGA.



(b) DTG.

Figure 5.10: Comparative TGA and DTG plots for uncoated and coated lime sludge – HDPE composites and pure HDPE.

lime sludge filled HDPE composites.

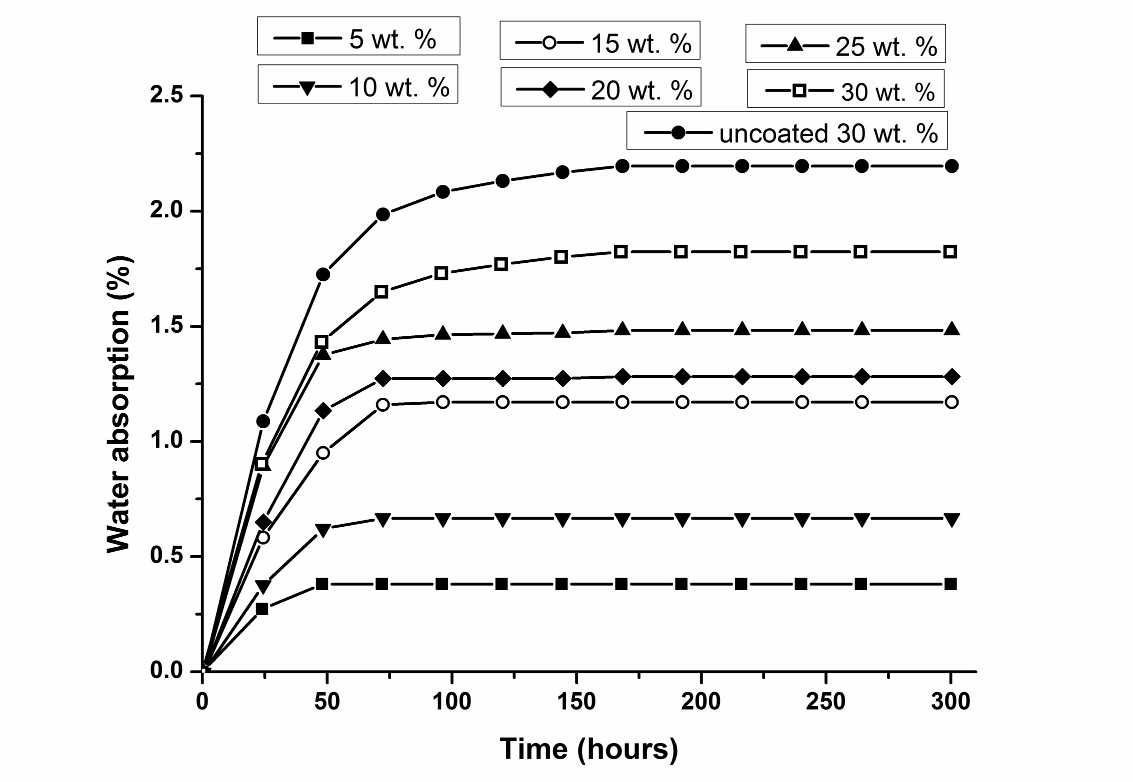


Figure 5.11: Water absorption *vs.* time for various filler loading of stearic acid coated lime sludge and 30 wt % uncoated lime sludge in HDPE composites.

5.5 Regression Analysis

Polynomial regression models containing higher order terms are developed for all mechanical properties - tensile strength (TS), tensile modulus (TM), elongation at break (EB), flexure strength (FS), flexure modulus (FM), and impact strength (IS), using the observed experimental data. The regression equations developed provided excellent fit for the variations of all mechanical properties as a function of stearic acid coated lime sludge filler in composites. The regression equations from Eq. (5.1) to Eq. (5.6) are provided below:

$$\mathrm{TS} = -30182\mathrm{x}^5 + 21159\mathrm{x}^4 - 6287.5\mathrm{x}^3 + 1064.4\mathrm{x}^2 - 92.795\mathrm{x} + 16.879; R^2 = 0.9908 \tag{5.1}$$

$$\mathrm{TM} = (1\times10^6)\mathrm{x}^5 - 862929\mathrm{x}^4 + 249285\mathrm{x}^3 - 26740\mathrm{x}^2 + 840.97\mathrm{x} + 139; R^2 = 0.987 \tag{5.2}$$

$$\mathrm{EB} = (-9\times10^{6})\mathrm{x}^{5}+(8\times10^{6})\mathrm{x}^{4}-(3\times10^{6})\mathrm{x}^{3}+386167\mathrm{x}^{2}-25812\mathrm{x}+806.24; R^{2} = 0.9423 \tag{5.3}$$

$$\mathrm{FS} = 14433\mathrm{x}^{5}-9813.4\mathrm{x}^{4}+3046.8\mathrm{x}^{3}-647.25\mathrm{x}^{2}+6.2386\mathrm{x}+806.24; R^{2} = 0.9987 \tag{5.4}$$

$$\mathrm{FM} = -269732\mathrm{x}^{4} + 186619\mathrm{x}^{3} - 45881\mathrm{x}^{2} + 5417.4\mathrm{x} + 247.49; R^{2} = 1 \tag{5.5}$$

$$\mathrm{IS} = -236108\mathrm{x}^{5} + 232632\mathrm{x}^{4} - 81697\mathrm{x}^{3} + 12209\mathrm{x}^{2} - 693.18\mathrm{x} + 30.007; R^{2} = 0.9992 \tag{5.6}$$

Similar to that of uncoated lime sludge-HDPE composites, it is found that for any specific wt % of coated filler, all the six properties vary differently and contradictorily. Hence, it is up to the manufacturer to choose the correct wt % of coated filler in order to obtain composites with the desired combination of mechanical properties.

Thus, Fig. 5.12 shows the consolidated image of the curves derived from Eq. (5.1) to Eq. (5.6). The Y-axis has been normalized so that all the mechanical properties lie in the range of 0 - 1. Using Fig. 5.12, based on the desired mechanical properties, a user will be able to determine the weight fraction of the stearic acid coated 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 13-14 MPa, then based on Fig. 5.12, a 12 wt % stearic acid coated 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 468 %, flexural strength of 10.5 MPa, flexural modulus of 498 MPa, and impact strength of 23 J/m for a 12 wt % filler composites must be considered beforehand (using Fig. 5.12), in order to ensure whether they satisfy the acceptable limits criteria for these parameters.

5.6 Comparison with popular theoretical models

The properties of particulate composites have been studied in detail over the years. Hence, numerous models have been developed which have tried to describe the ten-

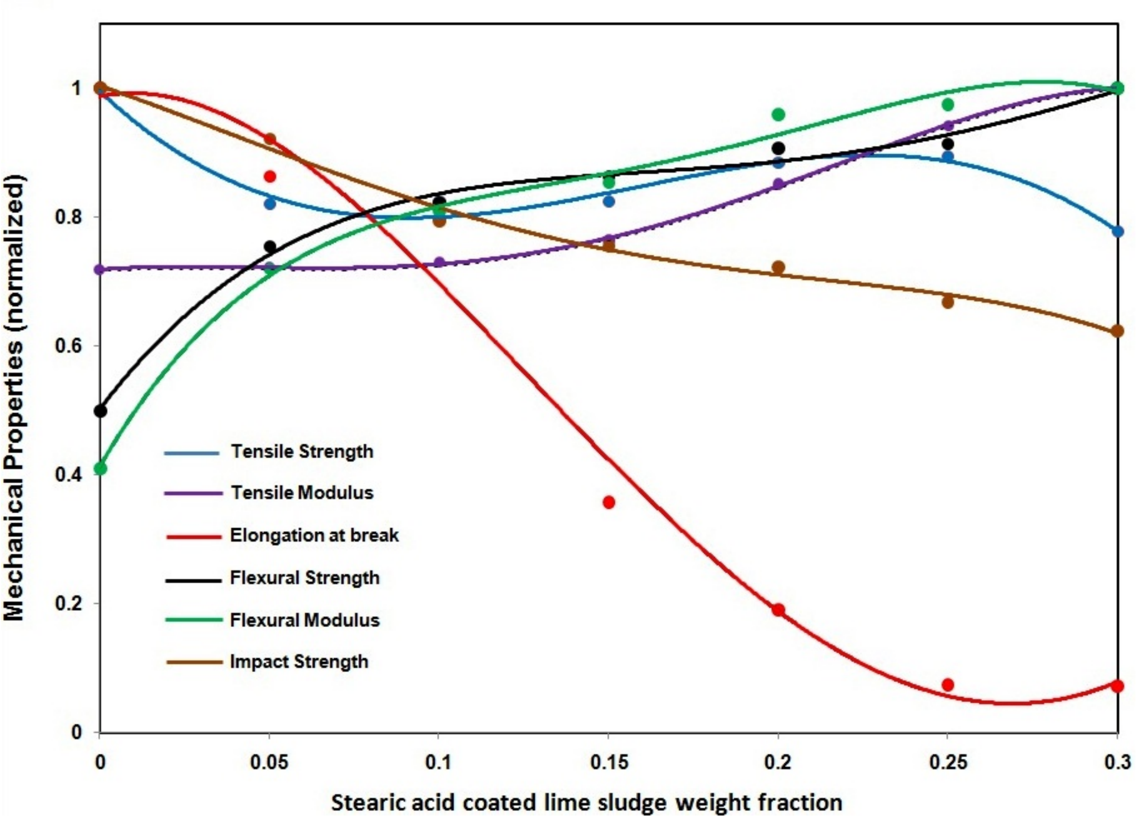


Figure 5.12: Normalized plot of mechanical properties as a function of stearic acid coated filler wt % obtained through regression analysis.

sile strength, tensile modulus and elongation of composite materials as a function of filler volume fraction. Modelling and simulation of composites are paramount in today's world due to the wide scale development of composites materials in engineering applications. The mechanical properties of particulate fillers are affected by parameters such as filler dispersion in the matrix, filler particle size, filler-matrix adhesion, filler volume fraction etc. Optimum mechanical properties ensure effective load transfer from the matrix to the rigid filler particles. Several theories have been forward over the years in order to relate the tensile parameters with the volume/weight fraction of filler added. In this section, the experimental results obtained through tensile tests for uncoated and stearic acid coated lime sludge-HDPE composites are compared with popular theoretical models proposed over the years, in a bid to correlate experimentally obtained values with theoretically obtained models.

5.6.1 Relative tensile strength

For comparing the experimental values with prominent theoretical models, the relative tensile strength (RTS) values were formulated using Eq. (5.7).

$$\text{RTS} = \frac{\sigma_c}{\sigma_{HDPE}} \tag{5.7}$$

where σ_c and σ_HDPE are the tensile strengths of composite and pure HDPE respectively. The volume fraction (ϕ_f) of lime sludge added is calculated using the Eq. (5.8). The density of lime sludge (ρ_1) is taken as 1.236 g/cm^3 as reported by Baruah and Borah earlier for lime sludge obtained from the HPCL paper mill at Jagiroad, Assam (lime sludge collected from this industry) [33]. The density for HDPE (ρ_2) is taken as 0.95 g/cm^3 as reported earlier in Chapter 3. $\mathrm{w_i}$ is the weight fraction of the $\mathrm{i^{th}}$ component in the composite.

$$\phi_\mathrm{f} = \frac{\frac{\mathrm{w}_i}{\rho_i}}{\sum\frac{\mathrm{w}_i}{\rho_i}} \tag{5.8}$$

The obtained experimental values of tensile strength are analysed using three mathematical models. The first model was formulated by Nicolais and Narkis [263], as given below in Eq. (5.9).

$$\text{RTS} = \frac{\sigma_c}{\sigma_{HDPE}} = 1 - 1.21\phi_\mathrm{f}^{(2/3)} \tag{5.9}$$

where σ_c and σ_HDPE represents the tensile strength of the composite and pure HDPE respectively. The results obtained from the model are also shown in Fig. 5.13. In case of stearic acid coated composites, the calculated RTS values do not match well with the experimental results since this model assumes no adhesion between matrix and filler. Similar trend was observed by Finkenstadt et al. [76] in which this model has been used to compare the amount of adhesion between oilseeds. However, the variation of experimental values for uncoated filler composites match with this model, suggesting that the there is minimal interaction between the filler and the matrix. This weaker interfacial adhesion results in the decreased tensile strength matched with the results determined using this model. Extremely low experimental values of tensile strength at 5 wt % lime sludge for uncoated filler is observed when compared with this model. At such a low filler content, the lime sludge particles act as inclusion dispersed at random locations rather than adding a reinforcing effect. Hence, such low tensile values are observed.

Subsequently, the experimental values are fitted with a second model proposed by Halphin-Tsai [263] given by Eq. (5.10).

$$\mathrm{RTS} = \frac{\sigma_c}{\sigma_{HDPE}} = \frac{1 + \mathrm{G}\eta_{\mathrm{T}}\phi_{\mathrm{f}}}{1 - \eta_{\mathrm{T}}\phi_{\mathrm{f}}} \tag{5.10}$$

where

$$\eta_{\mathrm{T}} = \frac{\mathrm{R_T} - 1}{\mathrm{R_T} + \mathrm{G}} \tag{5.11}$$

and

$$\mathrm{G} = \frac{7 - 5\nu}{8 - 10\nu} \tag{5.12}$$

Herein, $\mathrm{R_T}$ is the ratio between the tensile strength of filler to matrix, G is a constant and ν is the Poison's ratio of HDPE, taken to be 0.46. $\mathrm{R_T}$ was calculated by trial and error to match with the experimental results and was found to be 0.8. However, it is observed from Fig. 5.13 that this model does not match well with the experimental results as it assumes excellent adhesion between matrix and filler such that the RTS values obtained from this model varies only slightly with increasing volume fraction of filler addition.

The third model with which the experimental values are compared was proposed by Turcsanyi [49] given by the Eq. (5.13) below:

$$\mathrm{RTS} = \frac{\sigma_c}{\sigma_{HDPE}} = \frac{1 - \phi_{\mathrm{f}}}{1 + 2.5\phi_{\mathrm{f}}}\exp(\mathrm{B}\phi_{\mathrm{f}}) \tag{5.13}$$

where B is a constant depending on adhesion at the filler-matrix interface. Earlier, it was observed by Bliznakov et al. [49] that a B value of 0.25 indicates no adhesion, and the adhesion characteristics increase with increasing value of B. In another study, Zou et al. [285] obtained a higher B value of 3.44 for talc-polyesteramide composites exhibiting better tensile strength than calcium carbonate filled polyesteramide composites (B = 2.24). In the present case, as shown in Fig. 5.13, a B value of 1.4 for uncoated filler obtained by trial and error indicates lower adhesion between filler and matrix. While a B value of 2.21 for stearic acid coated filler indicates much better interaction at the filler-matrix interface. Thus, the Turcsanyi model fits moderately well with the experimental values of coated filler composites.

5.6.2 Relative Young's modulus

Restriction in the mobility of HDPE chains due to the addition of rigid lime sludge particles leads to the rise in the Young's modulus values. The variation in rela-

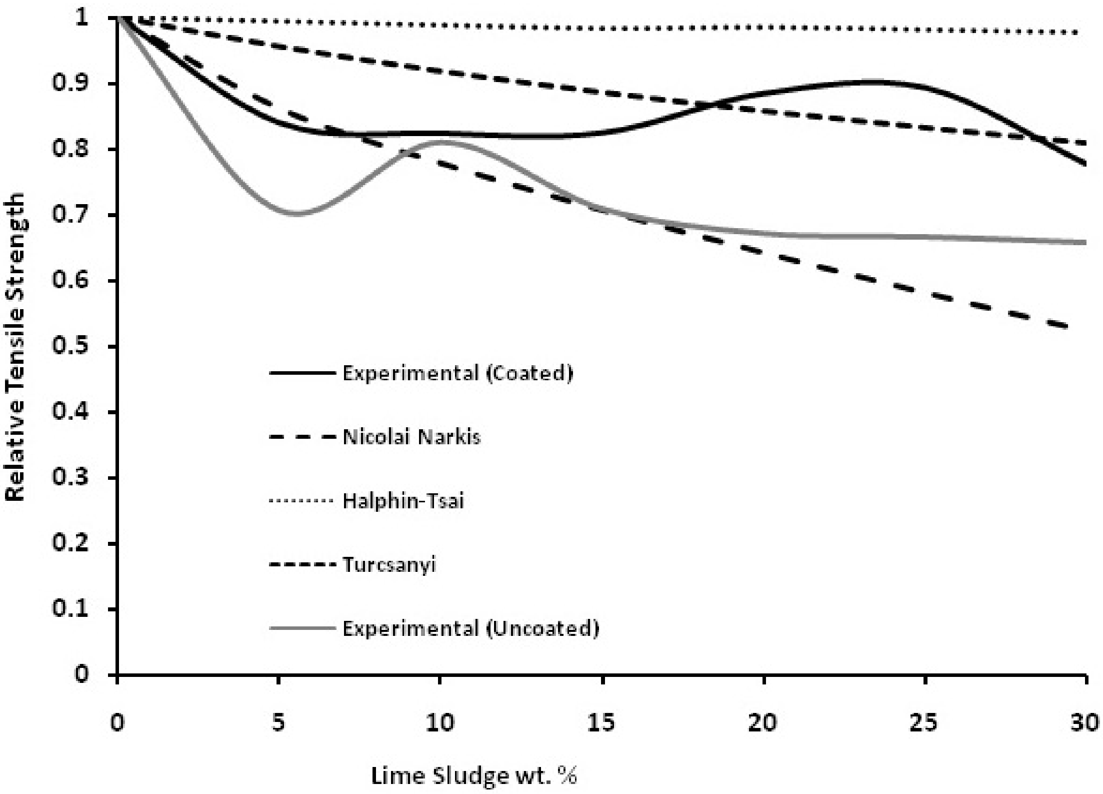


Figure 5.13: Relative tensile strength (RTS) as a function of lime sludge weight fraction.

tive Young's modulus (RYM) values as function of lime sludge wt. % is shown in Fig. 5.14. Four popular theoretical models have been used in order to analyse the obtained experimental values. The first model in consideration was proposed by Kerner [263] given by Eq. (5.14) below:

$$\mathrm{RYM} = \frac{\mathrm{E}_c}{\mathrm{E}_{HDPE}} = 1 + (\frac{\phi_\mathrm{f}}{1-\phi_\mathrm{f}})(\frac{15(1-\nu)}{8-10\nu}) \tag{5.14}$$

Where $\mathrm{E_c}$ and $\mathrm{E_{HDPE}}$ are the Young's modulus of the composite and pure HDPE respectively. It is observed that the experimental results do not match with this model as it assumes no interaction at the filler-matrix interface and does not consider any shape factor for particles in the composite.

The second model which accounts for good matrix-filler adhesion the Halphin-Tsai model [263] is given by Eq. (5.15) below:

$$\mathrm{RYM} = \frac{\mathrm{E}_c}{\mathrm{E}_{HDPE}} = \frac{1+\mathrm{G}\eta_\mathrm{m}\phi_\mathrm{f}}{1-\eta_\mathrm{m}\phi_\mathrm{f}} \tag{5.15}$$

where

$$\eta_\mathrm{m} = \frac{\mathrm{R_m}-1}{\mathrm{R_m}+\mathrm{G}} \tag{5.16}$$

Herein, R_m is the ratio of the filler modulus to the matrix modulus and is taken as 5.4 by trial and error in order to match the experimental results. Since, this model is valid for composites with good adhesion properties between the filler and the matrix, the results in this case, deviated significantly with increasing weight fractions of lime sludge due to weak interfacial adhesion at the filler-matrix boundary. Earlier, Praveen et al. [191] found good agreement between the experimental and theoretical values of nano-clay fillers in a rubber matrix which showed better adhesion at the filler-matrix interface.

The third model in consideration is the Sato-Furukawa model [233] given by Eq. (5.17). Herein, an adhesion parameter ξ is taken into account for the interaction at the filler-matrix boundary. ξ varies from 0 to 1 for perfect adhesion to no adhesion respectively.

$$\mathrm{RYM} = \frac{\mathrm{E}_c}{\mathrm{E}_{HDPE}} = [(1 + \frac{\phi_{\mathrm{f}}^{2/3}}{2 - 2\phi_{\mathrm{f}}^{1/3}})(1 - \psi\xi) - (\frac{\phi_{\mathrm{f}}^{2/3}\psi\xi}{(1 - \phi_{\mathrm{f}}^{1/3})\phi_{\mathrm{f}}})] \tag{5.17}$$

where

$$\psi = (\frac{\phi_{\mathrm{f}}}{3})[\frac{1 + \phi_{\mathrm{f}}^{1/3} - \phi_{\mathrm{f}}^{2/3}}{1 - \phi_{\mathrm{f}}^{1/3} + \phi_{\mathrm{f}}^{2/3}}] \tag{5.18}$$

Herein, ξ is found to be 0.5 and 0.6 by trial and error basis for uncoated and stearic acid coated lime sludge-HDPE composites. This indicates moderate adhesion at the filler-matrix boundary which coated filler being more interactive at the filler-matrix boundary. This was also indicated by the SEM micrographs where the lime sludge particles dropped out of the matrix due to weak interfacial adhesion especially a higher filler loading. Hence, the model and experimental values seem to deviate at higher filler loading in case of uncoated filler. However, the model suits well with coated filler composites at higher filler loading indicating effective reinforcement at higher filler loading of 25 wt %.

The experimental results are analysed with a fourth model proposed by Guth and Gold [93] which evaluates the reinforcing efficiency of filler particles using the volume fraction of filler particles. They introduced a quadratic term on the basis of the Smallwood-Einstein equation to take account of the interaction between filler particles, and obtained the following Eq. (5.19).

$$\mathrm{RYM} = \frac{\mathrm{E}}{\mathrm{E}_m} = 1 + 2.5\phi + 14.1\phi^2 \tag{5.19}$$

where E is Young's modulus of filled elastomer, E_m is matrix Young's modulus, and

ϕ is the volume fraction of filler. Eq. (5.19) is only applicable to elastomers filled with a certain amount of spherical fillers. If the filler concentration is higher than 10 vol %, the modulus increases much more rapidly than Eq. (5.19) would predict. This can be attributed to the formation of a network by the spherical filler chains. This model considers the hydrodynamic effect and mutual disturbance caused by spherical particles and allows predictions of properties at higher volume fraction of fillers [93, 261]. However, this model cannot take into account the changes in the shape of particles that may exist due to particle agglomeration.

Hence, a shape factor (α) was incorporated into the modified Guth model given by Eq. (5.20) which accounts for the aspect ratio (length/breath) of the particles introducing the 'accelerated stiffening' condition [92].

$$\mathrm{RYM} = \frac{\mathrm{E}_c}{\mathrm{E}_{HDPE}} = 1 + 0.67\alpha\phi + 1.62(\alpha\phi)^2 \tag{5.20}$$

This model suits thoroughly with the experimental values with α value of 1.2. As depicted in the SEM micrograph (refer Fig. 5.3B), the shape of lime sludge particles is closer to spherical i.e. (length/breadth ratio of 1) and the shape factor of 1 finds good agreement with it. Hence, the experimental and predicted values are in close conjunction with each other. In an earlier study, Saini et al. [220] applied the modified Guth model to waste paper powder in low density polyethylene composites and found the shape factor to be 3.48 with elongated rod-like structure.

5.6.3 Relative elongation at break

The experimental values of relative elongation at break (REB) are compared with the theoretical model proposed by Nielsen [263] given by the Eq. (5.21) below:

$$\mathrm{REB} = \frac{\epsilon_{\mathrm{c}}}{\epsilon_{\mathrm{HDPE}}} = (1 - \mathrm{k}\phi_{\mathrm{f}}^{1/3}) \tag{5.21}$$

where ϵ_{c} and ϵ_{HDPE} are the elongation at break parameters for the composite and pure HDPE respectively. In Eq. (5.21), k is a parameter depending on the filler geometry. The value of k is determined by trial and error and found to be 1.46. However, it was observed that the experimental values are greater than the predicted values at low filler loading while the predicted values are found to be higher with rising filler weight fraction. This is because the Nielsen model is based on perfect adhesion at the filler-matrix interface such that the polymer breaks at the same elongation in the filled system as in the neat polymer. It may be stated that at

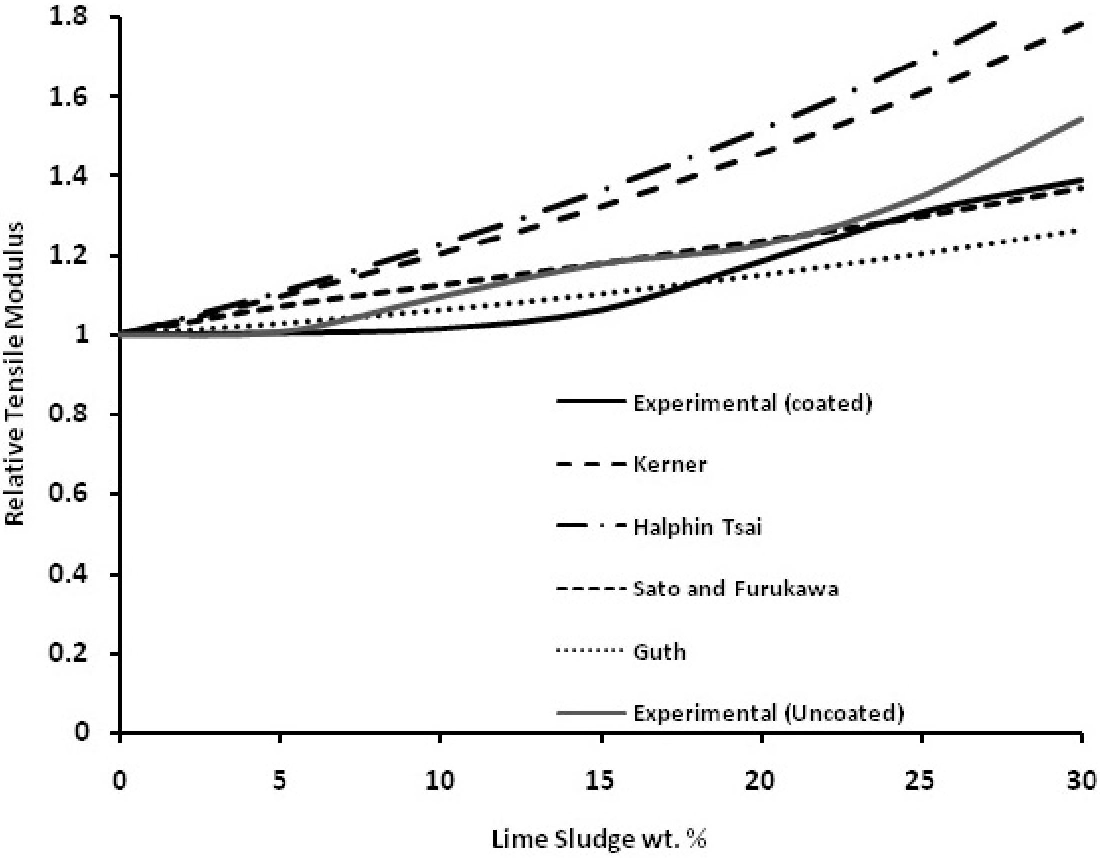


Figure 5.14: Relative Young's modulus (RYM) as a function of lime sludge weight fraction.

low filler loadings, the ductility effect of the polymer is much more prominent as the filler to filler inter-particle distances are much higher. While at higher filler loadings, parameters such as low inter-particle distances, particle agglomeration, and weak adhesion, lead to high stress concentration and subsequent, embrittlement of the composite. The Nielsen model was used by Deepthi et al. [66] in case of HDPE-flyash cenospheres where a k value of 1.3 for good adhesion; however, the obtained results did not match the model.

The comparative plots for experimentally obtained and Nielsen model of relative elongation at break are shown in Fig. 5.15.

5.7 Summary

It is observed in the previous chapter that raw (uncoated) lime sludge particles pose a stiff challenge in term of particle agglomeration at higher filler content leading to low mechanical properties. Stearic acid which would help in uniform dispersion of particles in the polymeric matrix hindering agglomeration, is used to surface coat

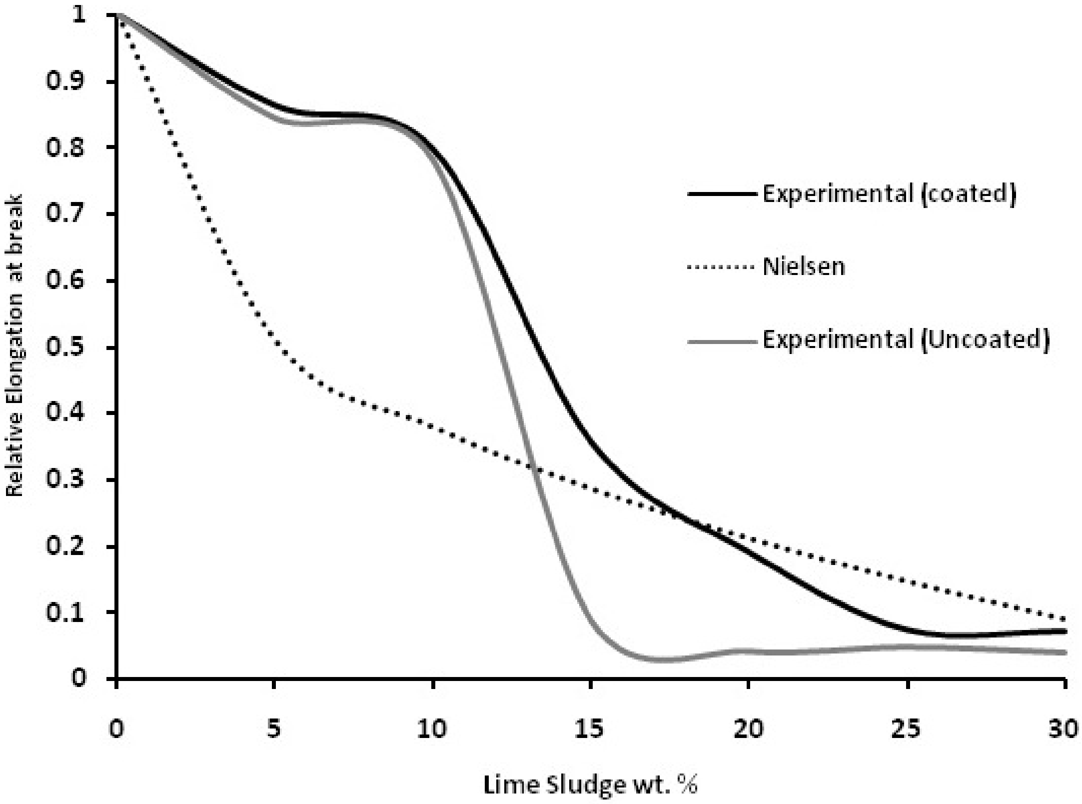


Figure 5.15: Relative elongation at break (REB) as a function of lime sludge weight fraction.

the lime sludge particles in this study. Subsequently, the coated lime sludge particles are used as filler in HDPE composites and their properties are compared with those of uncoated lime sludge filled composites and virgin HDPE. The summary of the chapter is as follows:

- Although the tensile strength of the composites decreased when compared with virgin HDPE, the tensile strength values for the stearic acid coated composites are found to be higher than that of uncoated ones. Additionally, the individual peak tensile strengths are observed at 10 wt % for uncoated (13.67 MPa) and at 25 wt % loading for coated (15.08 MPa) filler composites respectively. Better physical interaction and entanglement between the long hydrophobic chains of stearic acid moiety on the filler particles and HDPE chains result in better tensile strength. Moreover, stearic acid coating made the lime sludge particles hydrophobic in nature; thus, hindering their agglomeration and increasing their dispersion in the HDPE matrix.

- The tensile modulus (139.25 MPa for pure polymer to 193.75 MPa for 30 wt%) and flexural modulus (245.7 MPa for pure polymer to 193.75 MPa for 600 wt%) increased upon the addition of rigid lime sludge particles. This is due to the introduction of a mechanical restraint which causes restriction in the deformation within the elastic limit. However, the rigidity of stearic acid coated lime sludge composites are observed to be slightly lower than its uncoated counterpart because the mechanical restriction to chain mobility is more pronounced in case of uncoated filler composites.

- The ductility *i.e* elongation at break (806% for pure polymer to 58.4% for 30 wt%) and impact strength (30.2 J/m for pure polymer to 18.8 J/m for 30 wt%) values for coated composites although decreased, but are still higher than that of uncoated ones as the effect of particle agglomeration on ductility and impact toughness is less prominent in coated composites.

- The flexural strength of stearic acid coated composites (6.2 MPa for pure polymer to 12.5 MPa for 30 wt%) increased with increasing filler loading and is observed to be higher than uncoated composites due to the superior physical interaction and entanglement between the long hydrophobic chains of stearic acid moiety present on filler particles and the hydrophobic HDPE chains under bending stresses.

- TG analysis revealed a light weight loss between 250 °C and 400 °C associated with the degradation of stearic acid in case of coated filler composites. In case of uncoated filler composites it is found that the HDPE matrix decomposes in the range of 400 °C to 500 °C leaving behind $CaCO_3$ (which degrades to CaO) as residue. However, stearic acid coated filler composites decomposed above 600 °C due to the entanglement between the long hydrophobic chains of stearic acid moiety on the lime sludge particles and the hydrophobic HDPE chains which increases the thermal stability of the composites.

- The water uptake increased with increasing filler loading for stearic acid coated lime sludge filled composites with 30 wt % filler composite recording the highest water uptake of 1.8%. However, the water uptake of 30 wt % uncoated filler composite (2.2%) is much higher than its coated counterpart (1.8%) suggesting that particle agglomeration and higher filler content created higher surface area for water absorption for uncoated composites.

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

- The regression models of the tensile properties (tensile strength, tensile modulus and elongation at break) are compared with popular theoretical models proposed over the years, in a bid to model the experimental results in line with theoretical formulaes.