Chapter 3

XLPE based Inorganic Hybrid Nanocomposites: Polymer/Filler Interaction, Morphology, Mechanical, and Thermal Properties

Abstract:
This chapter focuses on the studies of XLPE/Al₂O₃ nanocomposites as a function of filler concentration and nanocomposites of XLPE with Al₂O₃, SiO₂, TiO₂, ZnO and clay with same filler concentration of 5 wt% as a function of filler type. Morphological, mechanical, thermal and swelling properties of surface treated Al₂O₃ nanoparticle reinforced XLPE nanocomposites were investigated. Studies on different properties elucidated the fact that, once the threshold limit is crossed, the particle-particle interaction dominates over the particle-matrix interaction and the properties showed a decreasing trend. The analysis of the polymer/filler interaction by estimation of network density, chemical cross-link density and the experimentally observed much higher mechanical properties compared to theoretical predictions confirm the topological constraints introduced by the filler particles (as shown in abstract graphic) on the XLPE chains. Also mechanical strength and thermal stability of spherical nanofillers of Al₂O₃, SiO₂, TiO₂, ZnO and clay platelets reinforced XLPE composites were investigated and compared.

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3.1 Introduction

Organic/inorganic hybrid nanocomposites have been extensively studied due to its great importance in different fields of life. The hybrid materials have the advantages of the inorganic material (e. g., rigidity, thermal stability) and the organic polymer (e. g., flexibility, ductility, processibility and dielectric properties) [1]. In this point of view, XLPE/inorganic filler nanocomposites are the best candidate for high performance materials. The nanofillers are able to produce a dramatic increase in interfacial area and thus a significant volume fraction of interfacial polymer with properties different from bulk polymer even at low loadings [2]. The properties of polymer composites depend on the interfacial adhesion between the matrix and the dispersed phase, properties of the matrix and the filler size, shape and content [3]. The nanocomposites exhibit enhanced mechanical and thermal behaviour which can be further explained by the morphology and the microstructure development by polymer/filler interaction.

The main challenge in the field of hybrid composites is that, it is difficult to disperse inorganic nanoparticles in polymers due to the incompatibility in surface characteristics between organic, hydrophobic, non polar polymer and inorganic, hydrophilic, polar nanofillers. The use of surface modification agents on nanofillers is required to reach a good dispersion of the filler in the polymeric matrix [4]. The exciting property improvements in polymer nanocomposites emphasize the critical role of the morphology and the interfacial region between polymer and filler [5]. In XLPE the interfacial polymer can exhibit changes in crystallinity, mobility, chain conformation, molecular arrangement and chain entanglement density [6]. Despite numerous investigations on XLPE filled systems, the molecular origin of the reinforcement effect is still under discussion. Several reinforcing factors have
been suggested in the literature to measure the predominance of filled systems over unfilled systems. The most important factors are the following: (i) a hydrodynamic effect due to the volume occupied by the filler, (ii) an elastically active network of nanoparticles, and (iii) the formation of a layer of immobilized polymer at the surface of the nanoparticles [7-8]. Nano hybrid assembling and the effective polymer/filler interaction leads to totally modified microstructure with altered chain dynamics, and this will contribute to the ultimate property enhancement of the system [9]. In well dispersed systems, it is possible for the interface zones to percolate through the entire nanocomposite, thus dominating bulk properties [10-11].

In this chapter, XLPE/surface treated Al₂O₃ nanocomposites at 0, 2, 5 and 10 wt% loadings of nanofiller and XLPE nanocomposites of Al₂O₃, SiO₂, TiO₂, ZnO and clay with 5 wt% nanofiller concentration were investigated. The synergistic effect of nanoparticles as fillers in XLPE, and the extent of polymer-filler interaction on property enhancement of nanocomposites are addressed.

3A: Studies on XLPE/Al₂O₃ Nanocomposites
3.2 Results and Discussion
3.2.1 Morphology: TEM
TEM images provide the most direct visualization of the state of dispersion of Al₂O₃ particles in the nanocomposites. A typical surface treated nanocomposite dispersion micrograph is shown in Figure 3.1. TEM observations indicate that similar composite structure is attained for all the three systems with good dispersion of nanoparticles in polymeric matrix. As the amount of nanoparticles increases from 2 wt% to 10 wt% the tendency for agglomeration also increases. The results suggest that dispersion may be improved when filler-filler interactions are reduced relative to filler-matrix interaction.
The two reasons for nanoparticle aggregation are (1) its inherent tendency to reduce the surface free energy, (2) the formation of hydrogen bonding due to the presence of OH groups. In this case the surface treatment on Al\textsubscript{2}O\textsubscript{3} nanoparticles, decreases the surface free energy as well as prevents the formation of hydrogen bonds between the nanoparticles during the preparation of the composite samples [12]. Another reason for obtaining good dispersion is that, the silane molecules used for surface treatment on Al\textsubscript{2}O\textsubscript{3} nanoparticles have a long alkyl chain, which has good compatibility with XLPE and enhance the adhesion between the filler and matrix. By the surface treatment on Al\textsubscript{2}O\textsubscript{3}, the nanoparticle surface becomes hydrophobic in nature (more organic and nonpolar character) and this will increase the compatibility with the matrix having similar surface properties [13]. Since XLPE and nano Al\textsubscript{2}O\textsubscript{3} are purely organic/inorganic system, both will be phase separated during the preparation. But the presence of alkyl group on nanoparticle act as a bridge between filler and polymer as the -OCH\textsubscript{3} part of trimethoxyoctyl silane will be chemically bonded to Al\textsubscript{2}O\textsubscript{3} and the octyl part will form linkage with polymer and this leads to the enhanced interaction between polymer and filler. The effect of surface treatment on interaction between organic polymer and inorganic nanoparticle is schematically represented in Figure 3.2 [14-15]. The alkyl chain on nanoparticle i.e., the organic tail of inorganic filler will interact with organic polymer. It is a vander Waal’s type interaction.
Figure 3.1: Transmission electron micrographs of (a) XLPE/2 wt% Al$_2$O$_3$ nanocomposite, (b) XLPE/5 wt% Al$_2$O$_3$ nanocomposite, and (c) XLPE/10 wt% Al$_2$O$_3$ nanocomposite.
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Figure 3.2: Schematic representation of increased interaction between the surface treated inorganic nanoparticle and organic polymer due to the presence of organic part on Al₂O₃ by surface treatment.

From the TEM distribution curves (Figure 3.3), it is evident that the increase in the amount of nanoparticles leads to more aggregation. This is explained by the predominant effect of particle-particle interaction over the particle matrix interaction at higher loadings of filler. Also as the wt% increases the distribution of particles become more broader.
Figure 3.3: Particle size distribution curves of XLPE/2 wt% Al₂O₃ (A2), XLPE/5 wt% Al₂O₃ (A5) and XLPE/10 wt% Al₂O₃ (A10).

3.2.2 Mechanical Behaviour

The stress-strain curves of XLPE and nanocomposites are shown in Figure 3.4. All the samples show a linear elastic behaviour followed by an inelastic plastic deformation. It can be seen that all the composites exhibit higher stress than the unfilled systems over the entire range of strain. Yield strength of XLPE and nanocomposites are compared as a function of filler concentration in Figure 3.5. While considering the different nanocomposites, upto 5 wt% the yield strength increases and then it decreases by further addition of nanofillers. In the case of nanocomposites, the presence of Al₂O₃ strengthened the polymer matrix, probably due to strong interfacial interaction between the components. A good interface will restrict the deformation of the polymer and which leads to the higher tensile strength value of the composite [16]. At the highest filler content, the observed decrease can be attributed to the predominant filler-filler interaction over
filler-matrix interaction where an insignificant stress transfer only occurs. The use of localized chemical reactions, enable the interaction of the organic group on the nano filler with the polymer matrix helps the homogeneous dispersion of the nanofillers and consequently the interfacial bonding and local load transfer could be enhanced which increases the elastic modulus and ultimate tensile strength when compared to the neat XLPE [17]. Also this is attributed to the higher degree of crystallinity of the composites in the presence of nano Al₂O₃, because of its ability to act as a good nucleating agent. These results indicated that the presence of the surface treatment on nanoparticle act as a link between polymer matrix and inorganic particles and provide an attractive interface and this improved the interaction of these two phases and compatibility, resulting superior mechanical properties [18]. Interfacial interaction determines the formation of effective nanophase and how the new nanophase constrains the surrounding polymers.

Young’s modulus of XLPE and nanocomposites are given in Figure 3.6. A significant increase in Young’s modulus is observed for the XLPE/Al₂O₃ nanocomposites at lower filler loading and then it shows a decreasing trend with an increase in nano Al₂O₃ content. It is understood that, an attractive interface will decrease the mobility of the polymer chains and a repulsive interface will increase the mobility [19]. Young’s modulus value is a direct indication of polymer chain dynamics. The polymer filler interaction can contribute towards physical network density. The immobilized polymer layer(constrained polymer) around the filler surface, is the direct result of the effective interaction between filler and polymer. This immobilized phase can contribute to the total network density of the polymer and thus the effective stress transfer in mechanical stretching, and increased modulus
value [20-22]. At higher filler loading, due to the filler aggregation, the formation of immobilized phase is not as efficient as at lower filler loading.

![Stress-Strain behavior](image)

**Figure 3.4**: Stress-Strain behavior of neat XLPE (X), XLPE/2 wt% Al$_2$O$_3$ nanocomposite (A2), XLPE/5 wt% Al$_2$O$_3$ nanocomposite (A5) and XLPE/10 wt% Al$_2$O$_3$ nanocomposite (A10).

![Yield strength](image)

**Figure 3.5**: Yield strength of XLPE (X), XLPE/2 wt% Al$_2$O$_3$ nanocomposite (A2), XLPE/5 wt% Al$_2$O$_3$ nanocomposite (A5) and XLPE/10 wt% Al$_2$O$_3$ nanocomposite (A10).
Figure 3.6: Young’s modulus of XLPE and nanocomposites as a function of wt% of nano Al₂O₃ content.

3.2.3 Thermogravimetric Analysis

Thermal degradation behavior of nanocomposites has been investigated by employing TGA analysis in N₂ atmosphere. TGA profiles of nanocomposites are presented in Figure 3.7. We can see that nanoparticles contribute to the rise of thermal degradation temperature. The maximum thermal stability has been achieved by introducing 10 wt% nano Al₂O₃. The thermal stabilization effect is mostly connected with the high thermal stability of Al₂O₃ nanoparticles and the extent of transfer of thermal energy from major phase to minor phase in a state of improved interface and better dispersion of nanofillers in polymeric matrix [23-24]. Since XLPE decomposition is through random chain scission, the cross-linked structure formed by DCP during melt processing speculated as an explanation for the improved thermal stability. The existence of nanoparticles facilitates recombination of the free radicals and raises
stable temperature regime close to 400 °C. Another possible explanation for the improvement of thermal stability is the formation of a nanoparticle layer on the surface of the polymer melt, which serves as a barrier preventing further degradation of the underlying polymer [25]. During the thermal degradation of polymer, the nanoparticles will accumulate to the surface of molten polymer creating a sort of shield that acts as physical protection from heat for the remaining polymer and slowing down the volatilization of the polymer fragments generated by the pyrolysis [26].

![TGA graphs of XLPE(X), XLPE/2 wt% Al₂O₃ nanocomposite (A2), XLPE/5 wt% Al₂O₃ nanocomposite (A5) and XLPE/10 wt% Al₂O₃ nanocomposite (A10).](image)

**Figure 3.7:** TGA graphs of XLPE(X), XLPE/2 wt% Al₂O₃ nanocomposite (A2), XLPE/5 wt% Al₂O₃ nanocomposite (A5) and XLPE/10 wt% Al₂O₃ nanocomposite (A10).

### 3.2.4 Differential Scanning Calorimetry

DSC results are summarized in Table 3.1. Percentage crystallinity and lamellar thickness is calculated using the equations given in Experimental section 2.3.3.2. Percentage crystallinity increases as the amount of nanofiller increases. This is due to the nucleation effect of nanofillers in
polymeric matrix. Nanofillers can act as heterogeneous nucleating agents in polymers, which leads to more ordered structure. In this case more number of small sized spherulites are formed. This explains the improved mechanical properties. There is not much change in melting temperature and in lamellar thickness. So we assume that more number of spherulites is formed but the lamellar thickness is not affected much by nanofillers [27-28]. The melting temperature is related to the crystal size while the enthalpy of fusion (area under the curve) is related to the total amount of crystallites. Cross-linking causes formation of new chemical bonds between the macromolecular chains and this hinders the crystal growth [29]. The cross-links play the role of defect centres, which impede the folding of macromolecular chains and thus the crystal size remains small.

Table 3.1: DSC results of XLPE and nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Melting Temperature (°C)</th>
<th>Crystallization temperature (°C)</th>
<th>ΔH J/g</th>
<th>% Crystallinity</th>
<th>Lamellar Thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>103</td>
<td>88</td>
<td>109</td>
<td>38</td>
<td>61</td>
</tr>
<tr>
<td>A2</td>
<td>102</td>
<td>90</td>
<td>121</td>
<td>43</td>
<td>59</td>
</tr>
<tr>
<td>A5</td>
<td>102</td>
<td>90</td>
<td>125</td>
<td>46</td>
<td>59</td>
</tr>
<tr>
<td>A10</td>
<td>103</td>
<td>89</td>
<td>127</td>
<td>49</td>
<td>60</td>
</tr>
</tbody>
</table>

3.2.5 Estimation of Network Density

Stress-strain behaviour of XLPE and XLPE/Al₂O₃ nanocomposites at 120 °C are shown in Figure 3.8. At 120 °C, above the melting temperature of XLPE, crystal structure is fully destroyed and the mechanical strength only depends on the network structure of the composites. Total network density is in direct correlation with the Young’s modulus (Table 3.2), i.e. the
slope of stress strain curve at 120 °C. Total network density is the sum of chemical cross-links and physical entanglements. Nanoparticles can contribute towards both chemical cross-links and physical networks by constrained polymer. The organic part in surface modification may also take part in cross-linking and in that case cross-link density will increase [16].

Network density can be further explained by the concept of rigid and constrained polymer phase. The immobilized polymer layer around the filler surface is the direct result of the effective interaction between filler and polymer. If the interaction between the filler and the amorphous phase is strong, a definite amount of constrained polymer fraction will generate. Polymer chain immobilization at nanofiller surface is schematically represented in the abstract graphic. Here the nanofiller surface is acting as an adsorption site and initiate the solidification process. Although, the number of these adsorption junctions is significantly smaller than the density of the chemical cross-links and the chain entanglements, this physical network has a significant indirect effect on the interface. First of all, the physical network junctions at the polymer-filler interface contribute to the total network density of the polymer [30-31]. Second, the polymer-filler interactions significantly increase the energy required to breakdown the nanoparticle aggregates during deformation. Finally, the physical junctions could dissipate energy during deformation, as a result of chain slippage along the filler surface and breaking and reaggregation of filler clusters [32]. We can conclude that, the reinforcing effect of filler in polymer is the sum of the enhancement of chemical cross-links, physical adsorption and improved interface.
Figure 3.8: Stress-Strain behavior at 120 °C of XLPE(X), XLPE/2 wt% Al₂O₃ nanocomposite (A2), XLPE/5 wt% Al₂O₃ nanocomposite (A5) and XLPE/10 wt% Al₂O₃ nanocomposite (A10).

Table 3.2: Young’s modulus at 120 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus at 120 °C (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>0.357</td>
</tr>
<tr>
<td>A2</td>
<td>1.92</td>
</tr>
<tr>
<td>A5</td>
<td>0.666</td>
</tr>
<tr>
<td>A10</td>
<td>0.400</td>
</tr>
</tbody>
</table>

3.2.6 Cross-link Density

Cross-link density was calculated from swelling experiments using Flory Rehner equation (Experimental section 2.3.4).
The cross-link density of XLPE and nanocomposites as a function of filler concentration is given in Figure 3.9. The cross-link density increases at lower nanofiller loading, afterwards it decreases. This is an indication of the reinforcing effect of nanofiller in the polymer matrix facilitating cross-linking mechanism until an optimum amount of nanofiller. The higher amount of nanofiller concentration interferes the cross-linking mechanism and the network structure formation is interrupted. The decrease in cross-link density at higher filler loadings can be attributed to the filler agglomeration at higher loading which causes a decrease in polymer–filler interactions. Also the immobilised polymer layer around the filler surface, the constrained polymer chain formation is restricted at higher filler loading due to the filler-filler aggregation process [33-35]. In the present system the nanofiller surface is modified with alkyl groups and thus there is a chance of increase in chemical cross-link density by

![Graph showing cross-link density as a function of filler concentration.](image)
taking part of alkyl groups on nanomaterials in cross-linking with polymer chains in the presence of cross-linking agent DCP.

The excellent mechanical properties and the changes in cross-link density as a function of filler loading can be further explained by the concept of rigid and constrained polymer phase around the filler surface. The immobilized polymer layer around the filler surface is the direct result of the effective interaction between filler and polymer. If the interaction between the filler and the amorphous phase is strong, a definite amount of constrained polymer fraction will generate. In the present system the nanofiller surface is acting as an adsorption site and initiate the solidification process. For this reason, they could be surrounded by an enriched layer of polymer with an increased modulus (high modulus layer), and around which a zone of material with a lower modulus (low modulus layer). So the mobile fraction in the original polymer is changed into two components, mobile and rigid ones. This immobilized phase can contribute to the cross-linking density of the polymer and thus the effective stress transfer in mechanical stretching process. The trend in cross-link density matches with earlier reported values. Putz et al. [36] emphasized that in the epoxy/MWCNT nanocomposites, cross-link density increases with MWCNT concentration and this can be attributed to the interphase creation leading to retarded dynamics, resulting in higher Tg. As the network density increases, the length scale of cooperatively rearranging regions (CRRs) decreases. This hinders communication of the dynamics between adjacent CRRs, thereby reducing inter phase penetration into the bulk matrix [37]. Similar results were reported by Xu et al. in the case of PU/ZrO₂ nanocomposites [38]. Both the increase in cross-link density and the grafting of polymer chains to a rigid nanoscale
reinforcement, enhances the molecular stiffness and thus the modulus of the nanocomposites. Bhattacharya and Bhowmick [20] reported that the addition of clay significantly modified the morphology of EVA by an increase in the immobile polymer fraction. The onset of such structure could be seen in light of percolation threshold–polymer chains are entangled with nanomaterials–forming a non mobile amorphous phase, which reduces the fractional crystalline morphology. As soon as crystals start to grow, they are surrounded by networks of constrained polymer layer and further growth is not possible. In the presence of nanomaterials heterogeneous nucleation starts, small crystal formation occurs and contributes towards total crystalline fraction, but crystal growth is disrupted by immobile polymer fraction around it [39]. Once the crystals are formed, less mobile constrained polymer formation dominates over the growth of the crystals. In a semi crystalline, filled system, there can be rigid amorphous fraction (RAF), crystalline fraction (CF) and mobile amorphous fraction (MAF) and the sum of the three fractions represent the entire polymer volume. Total rigid fraction RF= CF+RAF. Only the distribution of crystalline and rigid amorphous fraction changes as a function of filler content. Crystallization can proceed as long as certain mobility is present in the amorphous fraction of the sample. When this limit is reached during the crystallization process, main crystallization stops and no further growth is possible, most probably because transportation of crystallisable mobile amorphous material to the growth front becomes impossible due to large amount of constrained polymer around it [40]. We can conclude that, in the present system, crystalline fraction, constrained amorphous phase and mobile amorphous phase play roles in improving the microstructure in the presence of nanomaterials,
and thus the mechanical behaviour. Young’s modulus value of nanocomposites can be explained by the polymer immobilization by network structure formation, while Yield strength is the sum of crystalline morphology and constrained phase. The structural characteristics obtained by swelling studies correlates with the estimation of Young's modulus at room temperature and at 120 °C.

3.2.7 Theoretical Modelling

The mechanical properties of particulate filled composites are affected by various parameters such as filler shape, filler orientation and filler/matrix adhesion. The efficiency of load transfer from matrix to the filler in a composite is strongly related to the optimum mechanical properties. Among several theories, the most prominent models are Einstein, Guth, Thomas and Quemadi [41-42].

**Einstein Equation**

\[ E_c = E_p (1 + 2.5 V_f) \] \hspace{1cm} 3.1

Where \( E_c \) is the Young’s modulus of the composite, \( E_p \) is the Young’s modulus of the polymer and \( V_f \) is the volume fraction of the filler. This modelling is suitable for systems having non interactive spherical particles. Einstein’s equation implies that the stiffening or reinforcing actions of filler is independent of the size of the filler particles. This equation shows that the volume occupied by the filler is independent of the size of the filler particles, and its volume occupied by the filler, not its weight, is the important variable. This equation also assumes that filler is more rigid than matrix.
**Guth Equation**

\[ E_c = E_p (1 + 2.5V_f + 14.1V_f^2) \] ……………………3.2

Guth’s equation is an expansion of Einstein, to account for the interparticle interaction at higher filler loadings.

**Thomas Equation**

\[ E_c = E_p (1 + 2.5V_f + 10.05V_f^2 + 0.00273 e (16.6V_f)) \] …………..……….3.3

This equation is in agreement with a system having mono dispersed spherical particles. It doesn’t consider the inter particle interaction.

**Quemade Equation**

\[ E_c = E_p \left[ \frac{1}{(1-0.5K_6V_f)^2} \right] \] ………………………………………. ……..3.4

Where K is a constant normally 2.5. Quemade introduced a variable coefficient that signifies the particle interaction and its geometrical aspects.

The theoretical predictions have been plotted in Figure 3.10. It is seen that experimental values are higher than theoretically predicted ones for all the filler loadings. This indicates the existence of very strong interaction between XLPE and nanoparticle. From the mechanical properties we can see that there is considerable interaction between filler surface and the polymer matrix. At very low filler loading, the deviation is very high. This is due to the fact that at the lowest filler loading itself, reinforcing action is too strong. It is interesting to note that all the models gives better fitting at higher filler content. From the experimental observation, it can be understood that the change in polymer morphology, especially the presence of constrained polymer by physical adsorption of polymer chains on nanoparticles contribute much towards the total network density and chain dynamics of nanocomposites. This constrained zone or interfacial rigid amorphous zone retards the mobility of surrounding polymer chains
around filler surface. As explained in schematic representation (Figure 3.10) there is a possibility of (1) rigid zone, which is very close to nanofiller, (2) constrained zone, which is just after the rigid zone and (3) mobile zone, having free moving polymer chains, in nanocomposites [33-34,43]. However, none of the above models take into consideration of these aspects. As this micro structural change is predominant at lowest filler loading, it shows maximum deviation from the theoretical values. For the higher filler loadings, predominant filler/filler interaction inhibits a big change in morphology and thus the experimental values approach theoretical ones. At 2 wt% filler loading, nanofiller as a reinforcing agent and the changed morphology in the presence of nanofillers affect the modulus values. But as filler loading increases additional support from the morphological change is losing and only the effect of nanofillers remains. With this molecular structural model, the micro mechanics and the effect of the structure on the enhanced mechanical properties could be explored.

![Figure 3.10: Theoretical modelling of the Young’s moduli of XLPE/Al₂O₃ nanocomposites.](image-url)
3B: Mechanical Strength and Thermal Stability of XLPE Nanocomposites of Al₂O₃, SiO₂, TiO₂, ZnO and Clay Nanomaterials

3.3 Results and Discussion

3.3.1 Transmission Electron Microscopy

Transmission Electron Microscopy images of XLPE nanocomposites with different nanofillers of same concentration are compared in Figure 3.11. XLPE/Al₂O₃, XLPE/TiO₂ and XLPE/clay nanocomposites show better dispersion. In XLPE/SiO₂ and XLPE/ZnO nanocomposites, nanoparticle aggregation is more and large agglomerates are found. All nanoparticles are surface treated and in that way the incompatibility between organic polymer and inorganic nanofiller is reduced. The reason for the better dispersion of nanofillers in XLPE matrix is the organic link on the surface treated nanoparticle [14]. The inherent properties and surface free energy values of different nanofillers play roles in attaining the dispersion levels in the same system of XLPE matrix. Due to the variation in dispersion level, different nanocomposites arrive at different morphologies, which are able to tune different properties of the composites.
Figure 3.11: TEM images of XLPE with Al$_2$O$_3$ (A), SiO$_2$ (S), TiO$_2$ (T), ZnO (Z) and clay nanocomposites at 5 wt% filler concentration.

3.3.2 Mechanical Behaviour

Figure 3.12 compares the yield strength values of different nanocomposites of same filler concentration. The highlights of the results can be
summarized as follows: (i) All nanocomposites exhibit better yield strength values compared to the neat XLPE (ii) XLPE/Al$_2$O$_3$, XLPE/TiO$_2$ and XLPE/ZnO nanocomposites are mechanically stable compared to XLPE/SiO$_2$ and XLPE/clay nanocomposites (iii) XLPE/Al$_2$O$_3$ nanocomposite shows the best value of yield strength at 5 wt% filler concentration (iv) the strong aggregation tendency of silica nanoparticles and thus the heterogeneity in XLPE/SiO$_2$ system explains the reduced yield strength value of the nanocomposite (v) compared to three dimensional, spherical nanofillers, one dimensional nano clay platelets are less effective in reinforcing XLPE matrix. Young’s modulus values of different nanocomposites are given in Figure 3.13. As that of yield strength, all nanocomposites have better modulus compared to the neat XLPE. Enhancement in Young’s modulus is directly related to the polymer chain mobility [16-18]. Nanoparticles are able to reduce the chain mobility of the polyethylene and thus the nanocomposites exhibit better Young’s modulus values. Due to the effective interaction between polymer and nanofiller, XLPE/Al$_2$O$_3$, XLPE/TiO$_2$ show higher modulus values. The result is in correlation with the TEM results. XLPE/clay nanocomposites also have high modulus and this describes the role of polymer chains which are inside the clay platelets i.e. intercalated polymer chains in arresting polymer chain dynamics.
Figure 3.12: Yield strength of neat XLPE (X) and XLPE with Al₂O₃ (A), SiO₂ (S), TiO₂ (T), ZnO (Z) and clay (C) nanocomposites at 5 wt% filler concentration.

Figure 3.13: Young’s modulus of neat XLPE (X), XLPE with Al₂O₃ (A), SiO₂ (S), TiO₂ (T), ZnO (Z) and clay (C) nanocomposites at 5 wt% filler concentration.
3.3.3 Thermogravimetric Analysis

Figure 3.14 presents the TGA curves of neat XLPE and nanocomposites. The presence of fillers shifts the degradation temperature towards higher value, indicating higher thermal stability of the composites with respect to the neat XLPE. Inorganic nanoparticles possess higher heat capacity and thermal conductivity than XLPE, which means that the nanoparticles preferably absorbs heat, resulting the XLPE chains starts to degrade at higher temperatures [23]. Thermal energy is transferred from the major phase of polymeric matrix to the minor phase of nanoparticles during heating and the energy transfer will be efficient in a system with good interaction and effective interface.

![TGA graphs of neat XLPE (X), XLPE with Al₂O₃ (A), SiO₂ (S), TiO₂ (T), ZnO (Z) and clay (C) nanocomposites at 5 wt% filler concentration.](image)

**Figure 3.14:** TGA graphs of neat XLPE (X), XLPE with Al₂O₃ (A), SiO₂ (S), TiO₂ (T), ZnO (Z) and clay (C) nanocomposites at 5 wt% filler concentration.
3.4 Conclusions

In this work, the mechanical behaviour and thermal properties of XLPE/Al₂O₃ nanocomposites have been investigated with special reference to the amount of nanofiller and the micro structural development in nanocomposites in the presence of nanofillers. The results can be summarized as follows:

1. The TEM images provide the state of dispersion of Al₂O₃ particles in the nanocomposites.

2. The improved mechanical properties of nanocomposites established the mechanism of load transfer between major phase and minor phase by the combined effect of mechanical reinforcement by total network density and change in crystal structure.

3. The introduction of nanoparticles to the XLPE system contributes to the enhancement of thermal degradation temperature. The thermal stabilization effect is mostly connected with the high thermal stability of Al₂O₃ nanoparticles and the extent of transfer of thermal energy from major phase to minor phase in a state of improved interface and better dispersion of nanofillers in polymeric matrix.

4. The estimation of cross-link density and the stress strain behaviour at 120 °C and, the experimentally observed improvement in mechanical properties compared to theoretical predictions confirm the topological constraints introduced by the nanoparticles on the XLPE networks at lower filler loadings.
5. XLPE with 5 wt% of Al$_2$O$_3$, SiO$_2$, TiO$_2$, ZnO and nanoclay composites exhibit better mechanical strength and thermal stability.

6. While comparing, spherical nanoparticles and clay platelets, three dimensionally nano, spherical nanofiller reinforced composites show higher yield strength and thermal degradation temperature. Nano clay is effective in reducing the polymer chain mobility and thus increases the Young’s modulus value.

7. Among different spherical nanoparticle filled composites, XLPE/Al$_2$O$_3$ nanocomposite exhibits the best mechanical and thermal characteristics.

3.5 References


