CHAPTER-IV

RESULTS AND DISCUSSION
Chapter IV

4.0 Introduction

Present chapter briefly describes the result and discussion the following works,

1. Thermodynamic study of carbothermal reduction and nitridation of alumina in ammonia and argon plasma.
2. Synthesis and characterization of fine aluminium nitride powder using thermal plasma technique.
3. Synthesis and characterization of nano aluminium nitride powder using thermal plasma technique.
5. Sintering of plasma synthesized AlN powder and effect of sintering additive Y$_2$O$_3$ on sintering.
6. Fabrication of glass fiber- epoxy-AlN hybrid composites and study of its thermal, mechanical and electrical properties.
7. Fabrication of LLDPE/AlN composites and study of its thermal and mechanical properties.

4.1 Thermodynamic study of carbothermal reduction nitridation of alumina

Thermodynamic is a very useful tool in developing a new process or even for evaluating the possibility of optimizing existing processes. Thermodynamic calculations can establish the equilibrium conversion and composition for different conditions of temperature, pressure, type of reactants and reactant concentrations. The operating conditions needed to reach conversions at the desirable levels can be determined from these calculations. The reaction to be studied here is the solid-solid reaction of alumina and carbon in ammonia atmosphere to form solid aluminum nitride.

4.1.1 Thermodynamic Modeling

The objective of this modeling was to understand the thermodynamics of the reaction by which Al$_2$O$_3$, C, and NH$_3$ react to produce AlN at high temperatures. In order to understand the reaction mechanism of carbothermal reduction and nitridation of Al$_2$O$_3$ to AlN formation; MT
DATA commercial software developed by National Physical Laboratory (NPL), UK was used. The chemical equilibrium diagram for the Al-O-C-N-H-Ar system is shown in Figure 4.0. These graphs are plotted based on our experimental parameters.

4.1.2 Modeling Method

For this study, the reaction was simulated for 1 mole of Al$_2$O$_3$ (102 g) that reacts with 3 moles (stoichiometric ratio) or 6 moles (so as to simulate on excess of carbon) and 106.5 moles of nitrogen. Because, in most of experiments, 40 g of precursor material (Al$_2$O$_3$ : C $>$ 1 : 6) was used, this material was a mixture of 23.44 g of Al$_2$O$_3$ (0.23 moles) and $>$8.27g of C ($>$0.69 moles). In this study, we have also studied the effect of reduction of alumina without carbon in ammonia atmosphere. Ammonia gas was introduced into the furnace at a rate of 2 L/min for 0.5 h (total 60 liters of NH$_3$ gas = 2.678 moles (S.T.P). As stated above, this reaction was simulated for 1mole of Al$_2$O$_3$, therefore, the amount of N$_2$ gas used as input was106.5 moles (i.e. 24.5 moles N$_2$ / 0.23 moles Al$_2$O$_3$). Only 1 mole of nitrogen was consumed during the reaction, therefore the remaining nitrogen gas was 105.5 moles (106.5 moles – 1 mole) and the amount of CO gas produced was 3 moles. Based on the above calculation, the partial pressures of nitrogen and CO in the product gases can be calculated as follows: P(N$_2$) = 105.5 / (105.5 + 3) = 0.972 atm, and P(CO) = 3 / (105.5 + 3) = 0.0276 atm.

The solid-solid reaction between $\alpha$-Al$_2$O$_3$ and activated charcoal in NH$_3$ plasma is highly endothermic and thermodynamically possible at above 1450 K. The overall reaction is believed to proceed via two-step process.

From the chemical equilibrium diagram (Figure 4.0 b), it is observed that ammonia starts decomposing above temperature 300K in the 1st zone. However, in some literature[72], it is mentioned that the decomposition starts above temperature 473K (1st zone). Ammonia starts decomposing to form molecular N$_2$ and H$_2$ followed by the Eq. 4.1,

$$2\text{NH}_3(g) \rightarrow \text{N}_2(g) + 3\text{H}_2(g)$$ (4.1)

Above 700 K, NH$_3$ is completely dissociate in to N$_2$ and H$_2$ and helps in the nitridation of alumina in thermal plasma. According to experimental kinetics results [241] the decomposition is usually not fast enough to allow equilibrium to be achieved, particularly considering the residence time used to carry out the nitridation reaction in the experimental study.
Furthermore, since the dissociation of NH$_3$ is an endothermic and stepwise reaction, the temperature distribution in the reactor should be of important impact on the synthesis of AlN. A positive temperature gradient can provide driving force for the stepwise dissociation of N–H bonds and thus the formations of reactive nitrogen radicals become more favorable. It is also predicted that the synthesis of AlN is favored with a positive gradient of reaction temperature.
The effects of the temperature gradient and reaction temperature on the reduction nitridation of alumina powder in NH₃ gas flow are studied in detail.

4.1.3 Carbothermal reduction and nitridation of alumina

Overall reaction of the carbothermal reduction nitridation of alumina in ammonia plasma may be as,

\[
\text{Al}_2\text{O}_3(s) + 3\text{C}(s) + \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{AlN}(s) + 3\text{CO}(g) + 3\text{H}_2(g) \quad (4.2)
\]

It was assumed that the total pressure in the system was maintained at 1 atm. The formation of AlN is observed at temperature around 1450 K (2nd zone of Figure 4 a). As temperature increases, the conversion of Al₂O₃ to AlN is increases up to 2064 K. This is facilitated by decrease in the amount of Al₂O₃ and C (2nd zone of Figure 4 a) and N₂ (2nd zone of Figure 4 b) according to the Eq. (4.2). Above 2064 K (3rd zone of Figure 4 b), it has been seen that the amount of AlN and CO decreases and other species like Al₂O and N₂ are formed. Similar observations have been reported in the literature [242]. Above 2064 K, the following reaction is predicted

\[
2\text{AlN}(s) + \text{CO}(g) \rightarrow \text{Al}_2\text{O}(g) + \text{N}_2(g) + \text{C}(s) \quad (4.3)
\]

Above 2450 K (4th zone), possible reaction may be written as

\[
\text{Al}_2\text{O}(g) + \text{C}(s) \rightarrow 2\text{Al}(g) + \text{CO}(g) \quad (4.4)
\]

Although the equilibrium diagrams shown in Figure 4 indicate the trend of reactions and predicts the equilibrium composition of the final products, it cannot describe the actual kinetics and controlling mechanism of any particular reaction. However, these calculations provide useful guidelines for the chemistry in this process.

4.1.4 Advantage of of ammonia over nitrogen gas

N₂ and NH₃ are the gases commonly used as a nitrogen source for the production of AlN powder. The N – H bond energy in NH₃ is comparatively lower than the N – N bond energy in N₂, therefore less energy is needed to break the bond. The higher reactivity of NH₃ over N₂ is well recognized for this purpose and its use is preferred for carrying out short term reaction in
higher partial pressure of O\textsubscript{2} due to reducing atmosphere provided by ammonia [125]. These reactions were analyzed using the existing databases in the MTDATA software. Figure 4.1 shows the Gibb’s free energy of A-O-C-N-H system calculated by MTDATA software.

\textbf{Figure 4.1} Change in Gibb’s free energy as a function of temperature for Al-O-C-N-H system

Based on the thermodynamic study, the following conclusions can be drawn:

1. Positive $\Delta G$ values for sub oxide formation and low partial pressure of these species recludes their participation in the carbothermal nitridation process and it is extremely unlikely that they partake in any intermediate step in the reaction process.

2. There is no observation of possibility of formation of aluminum carbide/Auminum oxynitride/aluminumoxycarbide formation ($\text{Al}_4\text{C}_3$, $\text{AlC}$, $\text{AlON}$, $\text{Al}_4\text{O}_4\text{C}$ and $\text{Al}_2\text{OC}$) under the experimental conditions described in this thesis.

3. The ability to form AlN from $\text{Al}_2\text{O}_3$ is driven by the presence of NH\textsubscript{3} or N\textsubscript{2} gas which, under experimental conditions, flushes out the product gas (CO) and thus forces the
equilibrium in favor of AlN formation, assuming the $P(O_2)$ is maintained at a very low level.

4.1.5 Method of Calculation of Equilibrium composition

The calculation of equilibrium gas mixture compositions under condition of constant pressure was carried out using the method developed by White et al. [243]. It is based on the fact that the equilibrium of the system corresponds to its minimum energy state. The free energy, $G$, of the system is the sum of chemical potentials, $\mu_i$, multiplied by the mole fractions, $x_i$, of its components,

$$ G = \sum_{i=1}^{n} x_i \mu_i $$ (4.5)

where $n$ is the number of chemical species and $x_i$ their mole fractions to be determined. The set of $x_i$ values leading to the equilibrium can be obtained by solving the equation

$$ \delta G = 0 $$ (4.6)

under the fulfilled mass balance condition

$$ \sum_{i=1}^{n} \alpha_i x_i = b_j, j = 1, 2, 3, 4, \ldots, m. $$ (4.7)

where $m$ represents the number of elements in the system, $\alpha_i$ is the number of atoms of element $j$ in the molecule $i$, and $b_j$ is a coefficient proportional to the percentage of the element $j$ in the system. The quasi-neutrality of a system also containing charged species is ensured by the condition

$$ \sum_{i=1}^{n} q_i x_i = 0 $$ (4.8)

where $q_i$ represents the charge of species $i$. According to the method of White et al. [243], the mole fractions $x_i$ are calculated by an intractive procedure. One starts with any set of positive numbers $x_{i0}$ which satisfy Eqs. (4.7) and (4.8) and builds the zeroth-order approximation for $G$. The free energy is then expanded into a Taylor series up to the quadratic terms in $x_i - x_{i0}$. 

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The conditions (4.7) and (4.8) are taken into account with the help of Lagrange multipliers \( \pi_j \). A minimization of the free energy leads to a system of linear equations which determine the improved values for \( x_i \) and thus a new approximation for \( G \). The procedure is repeated until convergence is achieved. It should be noticed that the dimension of the system is \((m + 1)\), i.e. it depends only on the number of elements in the system. The concentrations of the species present in traces can be calculated using the Eq. 4.9:

\[
Z_i = \exp\left[-(G/RT)_i - \ln p + \sum_i \alpha_i \pi_i \right] \tag{4.9}
\]

Where ‘\( p \)’ is the total pressure of the system. Figure 4.2 shows the chemical potential of the components in Al-O-C-N-H-Ar system calculated by MTDATA software.

![Figure 4.2 Chemical potential of the Al-O-C-N-H-Ar system](image)

4.1.6 Mechanism of formation of AlN

It is thought that the rate of carbothermal reduction of \( \text{Al}_2\text{O}_3 \) is governed by solid state diffusion.
Therefore, the reaction time is dependent on diffusion distances, which for a large sintered agglomerate will be greater than for individually coated particles. This can be clearly shown in Figure 4.3 which represent the sequence of the solid-state diffusion of activated carbon particle in to the alumina particle. This is supported by the results of the reaction time study and morphology study discussed in later sections.

4.1.7 Vapour phase synthesis of ultrafine Particle

4.1.7.1 Gas-to-condensed phase transition mechanisms

Thermal plasma systems have been used here for the production of ultrafine particles mainly at a laboratory scale. According to the literature, determining the relationship between
particle size and process parameters is primarily empirical due to the complexity of plasma systems. The three routes which make possible the gas-to-condensed phase conversion are [244]:
— Homogeneous nucleation;
— Condensation on an existing particle;
— Heterogeneous chemical reaction on the surface of particles.

Each of these routes will be formulated next. The nucleation equation that considers the influence of surface reaction is briefly introduced in this section. Its detailed deduction is further presented in a separate section.

At high temperature of thermal plasma, AlN will form in the zone of the plasma reactor where gases have temperature lies from 1450 K to 2450 K and vaporized [245]. Particle growth of AlN can be possible due to homogeneous nucleation via vapour deposition on the particle surface or growth by collision and coalescence of particles (nuclei) [110]. The particle generation processes are described by the Aerosol General Dynamic Equation [246]. Particle transport results from processes such as bulk flow, brownian diffusion and effects of external force fields. These are referred as external processes since they involve the movement of particles across the wall of an elemental volume. The particle transport processes are described by the particle-number continuity equation, in the spatial coordinate system. In this equation, the internal processes are written as source terms.

The gaseous AlN vapour was transported to the water cooled chamber and top cover of the reactor due to thermophoretic effect and condensed to form solid nano particles. The nucleation rate of AlN particles is described by kinetic approach to the homogeneous nucleation theory [247]. The growth of AlN nuclei as nonorods based on the anisotropy of its wurtzite crystal structure under the driving force of the minimum surface free energy. When volatile species react to form condensed form, the rate of surface reaction increases significantly as a result oxidation of the AlN power cannot be avoided if the reactor is not fully purged with nitrising gas NH$_3$ and plasma forming gas Ar before reaction carried out.

The aerosol general dynamic equation for formation of AlN particle through simultaneous nucleation, condensation, and coagulation from an ideal super saturated vapour [247] can be written as
\[ I_{kin} = v_l (2\sigma/\pi m_l)^{1/2} \nu_s^2 S \exp \left[ \theta - \frac{4\theta^3}{27 \ln S} \right] \]  

(4.10)

Where, \( v_l \) is monomer volume (m³),
\( \sigma \) is surface tension (N/m),
\( m_l \) is mass of a monomer (kg),
\( \nu_s \) represents the equilibrium monomer concentration for a saturated vapour (m⁻³),
\( S \) is the super saturation ratio,
\( \theta \) is a dimensionless surface energy \( (\sigma S_l/(k_B T)) \)
\( T \) is the temperature (K),
\( S_l \) is the surface area of a monomer (m²), and
\( k_B \) is Boltzmann's constant (J/K).

The authors [247] consider all the classical theory assumptions, except that regarding the equilibrium state to which the evaporation should be referred. The assumptions of the classical theory are:

- Surface tension is size-independent (capillarity approximation),
- the clusters are spherical and charge neutral,
- mass accommodation equal to unity,
- the London Vander Waals force is neglected, and
- the system is sufficiently dilute that evaporation coefficients depend only on cluster properties and on temperature.

The two-dimensional model describing the aerosol particle size evolution was applied to the production of aluminum nitride powder, using the following assumptions:

- AlN condenses directly into the solid phase,
- the particles are assumed spherical, in the free molecular regime and the coefficient of coalescence is equal to unity.
- vapour condensation of the particles is considered for \( K_n > 0.2 \),
- the mean particle flow deviates from the gas streamlines by the thermophoretic force,
- particle Brownian diffusion is considered, and
- particles are assumed to be at the gas temperature.
4.2 Synthesis of fine AlN powder using thermal plasma technique

4.2.2 Effect of flow rate of ammonia gas

Rate of flow of ammonia gas play a vital role in the synthesis process of AlN in plasma. We have carried out different experiment varying the flow rate of nitriding gas ammonia from 0.5 L/min to 2 L/min with an interval of 0.5 L/min.

![XRD patterns](image)

It is observed from XRD report (shown in Figure 4.4) that the conversion of alumina to AlN is possible at flow rate 0.5 L/min of ammonia gas in high temperature of plasma zone. However, the complete conversion is possible at flow rate of 2 L/min. On increasing the flow rate, there is no substantial effect on the yield of AlN.

Figure 4.4 XRD patterns of plasma synthesized powders treated in different ammonia flow rate (a) 0.5, (b) 1, (c) 1.5, and (d) 2 L/min [Plasma parameter: load voltage – 50 V, current – 300 A and time and 25 min respectively]
4.2.3 Effect of variation of dc arc current

Figure 4.5 shows the XRD pattern of the plasma synthesized product synthesized with different load current varying from 150 to 300 A with interval of 50 V. As the current increase, the temperature of plasma changes increases accordingly, which was measured by optical pyrometer. The approximate temperature of outer zone of plasma is found to be about 1500–1800 °C. Higher load current causes the more ionization of plasma forming argon and nitriding NH₃ gas. All the experiments were carried out at different arc current from 150 to 300 A at 50 V with the interval of 50 A. From the XRD data, it has been clearly seen that maximum conversion of reactant occurs at load current of 300 A.

![XRD Patterns](image)

Figure 4.5 XRD patterns of plasma synthesized powders treated at various load current (a) 150, (b) 200, (c) 250 and (c) 300 A at 2 L/min ammonia flow

4.2.1 Effect of reaction time on the conversion of alumina into fine AlN

Figure 4.6 shows the XRD patterns of the plasma processed products at different time of processing along with the staring material alumina. Although the formation of AlN is observed after 5 min. of plasma processing, appreciable amount of AlN formation is only observed after 10 min of processing time.
Figure 4.6 XRD patterns of the plasma synthesized products at various processing time: (a) 0 min (Al₂O₃ powder), (b) 5 min, (c) 10 min, (d) 15 min, (e) 20 min and (f) 25 min

In 25 min. of processing, entire alumina is converted to AlN. All the peaks are attributed to hexagonal AlN which are in good agreement with JCPDS index card no. 25-1133. Lattice parameter (a = 3.11689 Å, c = 4.99253 Å) was calculated by using software Unit Cell [235]. The carbon peak is also observed in the XRD pattern. The presence of excess carbon in the product is due to the fact that we have used more carbon than the stoichiometric requirement of carbon content for formation of AlN. The presence of excess of carbon in the precursor material may
have facilitated intimate mixing of alumina with carbon and the synthesis of AlN powder with fine particle size [103]. Figure 4.7 (a) shows the XRD pattern of carbon free AlN powder.

![XRD pattern](image)

Figure 4.7 XRD pattern (a) of carbon free plasma synthesized AlN powder and (b) its photograph

### 4.2.4 Recovery of plasma synthesized product versus time

Figure 4.8 shows the weight of plasma synthesized product in various synthesis time from 5 min to 30 min. It was observed that the recovery at 5 min of processing time was maximum which contains mainly unreacted alumina and residual carbon. As the processing time increased, the recovery gradually decreased up to reaction time of 15 min. Again the recovery increases at 20 min of synthesis time due to the formation of AlN. After then the recovery become almost constant.
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Figure 4.8 Weight of recovery of plasma synthesized sample from 50 gm of starting material with different reaction time

4.2.5 Morphology analysis

Figure 4.9 SEM of (a) raw material alumina and FESEM image of (b) plasma synthesized fine AlN powder and its corresponding EDAX spectrum

The as-obtained powders are loosely agglomerated, well faceted and spherical in size which clearly visible in the FESEM report (Figure 4.9 b). The average particle size is about 5 – 7 µm.
Because of weakly aggregation of the elementary particle, the crude AlN powder, however, is easy to de-agglomerate by milling. The synthesized powders do not reflect the original morphology of raw alumina which is shown in Figure 4.9 (a). The presence of little carbon limits the agglomeration and prevents the growth of aggregates. The EDS profile of the as-produced AlN shows the presence of aluminium and nitrogen at 1.5 and 0.4 keV respectively. Very little oxygen impurity at 0.5 keV may come from the surface contamination (due to presence of moisture in air) which is inevitable for hexagonal AlN [249]. A thin layer of amorphous aluminium hydroxide may be formed on the surface of particle which cannot detect in XRD analysis.

4.2.6 Compositional analysis

![Figure 4.10 EPMA micrograph showing Al and O concentration in raw material alumina](image)

The compositional analysis was carried out by electron probe micro analysis (EPMA). Figure 4.10 shows the EPMA micrograph of raw material alumina. It shows the concentration of Al and N in different colour contrast. Figure 4.11 shows EPMA micrograph of AlN powder synthesized in 25 min through the cabothermal reduction of alumina in ammonia (2 L/min) and argon (1 L/min) plasma applying load voltage 50 V and load current 300 A. It shows the incorporation of element Al and N in the plasma synthesized powder in proper ratio. It is observed that the concentration of nitrogen is more in comparison to the concentration of oxygen.
Figure 4.11 EPMA micrographs and X ray mapping of plasma synthesized AlN powder synthesized in 25 min

4.2.7 Raman analysis

Figure 4.12 shows the raman spectra of the AlN powder. The space group of wurtzite AlN is $C_{6h} (p63mc)$ with all atoms occupying the $C_{3v}$ sites, having six active Raman modes such as $A_1$ (TO) + $A_1$ (LO) + $E_1$ (TO) + $E_1$ (LO) + 2$E_2$ in the spectrum. Out of six Raman-active phonon modes, only three peaks at 611.628, 655.619, 667.477 cm$^{-1}$ are indexed to active raman phonon mode of $A_1$(TO), $E_2$ (high) and $E_1$ (TO) respectively. Other phonon modes were not visible due to low intensity. The peaks are good agreement with the hexagonal AlN reported in literature [250]. High intensity of the $E_2$ (high) peak implies the good crystallinity of the plasma synthesized AlN powder [251].
4.2.8 Fourier Transformation Infrared red Spectroscopy (FTIR)

FTIR spectra (as shown in Figure 4.13) measure the structure and composition of AlN powder. The peaks of 1357, 520 cm\(^{-1}\) correspond to AlN while other peaks at 3449, 766, 1005, 1386 and 1595 cm\(^{-1}\) are from impurity. The peaks at 3449 and 1595 cm\(^{-1}\) are vibrational mode of O-H and the peak at 1386 cm\(^{-1}\) is swing vibrational mode of O-H. The peaks at 1005 and 766 cm\(^{-1}\) are swing vibrational mode of Al(OH)\(_3\). The hydrolysis of sample might have been occurred in the FTIR studies as the samples were characterized long time after synthesis. In some papers 1005 cm\(^{-1}\) recognized as the TO phonon of cubic AlN [109]. Although, cubic AlN is unstable the formation of cubic AlN may not be ruled out due to high quench rate associated with thermal plasma synthesis process. However, the XRD pattern does not show the presence of cubic AlN. Hence, no definite conclusion may be made in this regard. The cubic AlN if at all present in the plasma synthesized product may be available in very small quantity.

Figure 4.12 Raman spectra of carbon free Plasma synthesized AlN Powder
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Figure 4.13 FTIR absorption spectra of plasma synthesized AlN and raw alumina powder

4.2.9 Comparison of thermal conductivity of AlN powder with alumina

The variation of temperature in AlN and Al₂O₃ powder with time is illustrated in Figure 4.14.

Figure 4.14 Variation of temperature in AlN and Al₂O₃ powder with time
From the graph, it is observed that the rate of rise of temperature in AlN powder is more than the alumina powder. Hence, it is concluded that as-synthesized AlN powder is better conductor of heat than alumina.

4.3 Synthesis of Fine AlN Powder using N₂ and Ar Plasma

In this work, we have also carried out the same experiment i.e. carbothermal reduction of alumina in nitrogen atmosphere in the same reactor. The effect of plasma processing time on the conversion of alumina in to AlN has been studied.

4.3.1 Effect of Variation of Plasma Processing time

Figure 4.15 XRD patterns of the plasma synthesized product of different processing time from 5 minute to 30 min in N₂ / Ar plasma (using Co target)

Figure 4.15 shows the X-ray diffraction pattern of the plasma synthesized product varying processing time from 5 min to 30 min nitrogen plasma. From the XRD pattern, it is obvious that very small amount of alumina which are remained in the final product, are not converted into
AlN in nitrogen atmosphere. The typical plasma operating condition (Table 3.1), taking N\(_2\) gas for nitriding gas except ammonia for the full conversion of alumina in to AlN was adopted for Some unreacted alumina still remain in the final product after 30 min plasma processing at load current – 300 A & load voltage – 50 V. The reason may be attributed to the fact that nitrogen gas does not provide reactive atmosphere for reduction and nitridation of alumina [125]. Hence many researchers use mixture of N\(_2\) and other H\(_2\) containing gas instead of plain N\(_2\) gas for carbothermal reduction and nitridation of alumina [98].

### 4.3.2 Morphology

Figure 4.16 shows the morphology of the AlN powder synthesized in nitrogen plasma. It is observed that plasma synthesized powders are crystalline and loosely agglomerated. However, it can be de-agglomerate by milling. Figure 4.16 (c) shows the agglomerated body composed of small particles.

![SEM micrographs of AlN powders synthesized in nitrogen plasma](image1)

**Figure 4.16 SEM micrographs of AlN powders synthesized in nitrogen plasma**

Sample obtained from the surface of the top electrode are shown in Figure 4.16 (b) which looks like thin layer of AlN staked one over another.
4.4 Synthesis of nano-AlN powder using thermal plasma technique

4.4.1 Phase equilibrium and Thermodynamics

The phase equilibrium and thermodynamics of the reaction system in thermal plasma was studied using MTDATA phase diagram software developed by National Physical (NPL), UK. The solid-solid reaction between $\alpha$-$\text{Al}_2\text{O}_3$ and graphite powder in NH$_3$ plasma via carbothermal reduction reaction produces AlN. This reaction is highly endothermic and thermodynamically possible at temperature above 1450 K [104]. The details of the mechanism of the carbothermal reduction of alumina in ammonia/argon plasma are already discussed in previous section of this chapter.

4.4.2 Vapour phase synthesis of ultrafine particles

At high temperature of thermal plasma, nano particles of AlN will form in the zone of the plasma reactor where gases have temperature lies from 1450 K to 2450 K via homogeneous nucleation [245]. After nucleation, growth of AlN particle can be possible due to vapour deposition on the particle surface or growth by collision and coalescence of particles (nuclei) [110]. The gaseous AlN vapour was transported to the water cooled chamber and top cover of the reactor due to thermophoretic effect and condensed to form solid nano particles. The formed AlN nuclei can grow in different structures like nono particles, nano rods, nano tubes, nano fibers etc. based on the anisotropy of its wurtzite crystal structure under the driving force of the minimum surface free energy. When volatile species react to form condensed form, the rate of surface reaction increases significantly as a result oxidation of the AlN power cannot be avoided if the reactor is not fully purged with nitriding gas NH$_3$ and plasma forming gas Ar before reaction carried out.

4.4.3 X-ray diffraction studies

Figure 4.17 shows the XRD pattern of the nano AlN powder obtained from inner chamber wall and graphite crucible of the reactor. It is obvious that the powder obtained from inner chamber wall were fully converted into AlN whereas the powder obtained from crucible contained significant amount of Al$_2$O$_3$. The reason may be due to insufficient heat at the bottom of the inner crucible as it is placed in open space of the reactor and some of the precursor
materials were flown towards the crucible through the outer zone of the plasma where temperature is insufficient for nitridation of alumina. The powder sample obtained from crucible was mostly micron sized. When the precursor materials passed through the core of the arc plasma, it get easily converted into solid AlN, vaporized and deposited on the wall of the chamber and top cover. All the peaks in pattern of XRD of sample obtained from chamber are attributed to hexagonal AlN with lattice parameter of $a = b = 3.152 \, \text{Å}$ and $c = 4.953 \, \text{Å}$ with lattice volume $42.625 \, \text{Å}^3$ which are good agreement with JCPDF No 08-0262 [234].

![XRD pattern of nano AlN powder obtained from crucible and chamber wall of the reactor](image)

Figure 4.17 XRD pattern of nano AlN powder obtained from crucible and chamber wall of the reactor
The lattice parameters were calculated using software Unit cell [235]. The broadness of all peak indicated the formation of nano sized AlN particle. The miller indices of the crystallographic plane corresponding to peaks are marked. No other peaks except graphite were detected in the XRD pattern, which indicates that the products obtained from the chamber were pure nano AlN. Average crystallite size \( D_{hkl} \) was determined using full-width at half maximum (FWHM) of the two main peaks assigned to (110) and (110), estimated to be about 13 nm using Scherer formula [233] as given in Eq. (4.11):

\[
D_{hkl} = \frac{k\lambda}{\beta \cos \theta_{hkl}} \tag{4.11}
\]

Where,

\( D, \lambda, k, \theta \) and \( \beta \) are the average particle size, wave length of X-ray, shape factor (~0.94), Bragg angle and FWHM of the (hkl) diffraction peak respectively.

4.4.4 Morphology Study by FSEM and TEM

The morphology of the as-synthesized product was observed by FESEM and TEM. The typical FESEM and TEM image is given in the Figure 4.18 and 4.19. From both the images, it is observed that the particles are spherical in shape, loosely agglomerated and nano order in size. Powders are tend to form small agglomerates which are tends to resolve into individual particles with different size in nano order scale. Due to high temperature of thermal plasma, aggregates are formed because of sintering of primary particles during synthesis process. The corresponding EDAX of FESEM images show the presence of elemental Al, N, C and O. The presence of oxygen in the form of amorphous AlOOH [60] in plasma synthesized product may be due to surface contamination with moisture present in air. The aggregate often have fractal like branched structure with different dimensions like hexagon, spherical or rod etc. From TEM picture, it is also clearly visible the formation of nano rod through one dimensional growth of particle from the nucleation site. The selective area diffraction pattern (SAD) of AlN is shown in Figure 4.19. All the diffraction rings can be indexed to the hexagonal AlN which confirms the plasma synthesized powders are well crystallized.
Figure 4.18 Field emission scanning electron microscopy and its corresponding EDAX of plasma synthesized sample obtained from (a) crucible, (b) chamber of the reactor and (c) tip of top electrode
Figure 4.19 TEM image of nano sized AlN powder and its corresponding SAD pattern

4.4.5 Compositional analysis

Figure 4.20 Electron probe microscopy analysis of nano AlN powder obtained from chamber of the reactor

The compositional analysis of as-produced plasma synthesized AlN powder was studied under electron probe scanning electron microscope (EPMA) (Figure 4.20). This confirms the
incorporation of Al and N in the plasma synthesized product. The EDAX profile of the as-produced AlN exhibited the presence of aluminium and nitrogen at 1.5 and 0.4 keV respectively. A trace amount of oxygen impurity at 0.5 keV may come from the surface contamination (due to presence of moisture in air) which is inevitable for hexagonal nano sized AlN powder [249].

4.4.6 BET surface area analysis

The Specific surface area of a powder refers to the developed surface per unit of mass. It reflects the shape of the particles and roughness of their surface. The comparison between the specific surface area and the measured size of the particles informs us about the state of agglomeration of the powder. The grain size measurement technique takes into account the porous agglomerate, whereas the specific surface measurement takes in to account the surface of the particles constituting these agglomerates. Specific surface area can vary from a few tens of cm$^2$gm$^{-1}$, the average value of commonly used ceramic powders ranging between 3 and 15 m$^2$gm$^{-1}$. The higher the specific surface of a powder, the stronger the tendency to agglomeration, but the greater the sintering activity.

![BET surface area plot of plasma synthesized nano AlN powder](image)

**Figure 4.21** BET surface area plot of plasma synthesized nano AlN powder

The BET surface area was calculated using the formula,
\[
\frac{1}{Q((p/p_0) - 1)} = c - 1 \left( \frac{p}{p_0} \right) + \frac{1}{Q_m c} \quad (4.12)
\]

Where \(P\) and \(P_0\) are the equilibrium and saturation pressure of adsorbates at the temperature of adsorption \(Q\) is the weight of gas absorbed and \(Q_m\) is the monolayer adsorbed gas quantity. \(C\) is the BET constant,

\[
c = \exp \left( \frac{E_1 - E_L}{RT} \right) \quad (4.13)
\]

Where \(E_1\) is the heat of adsorption for the first layer, and \(E_L\) is that for the second and higher layers and is equal to the heat of liquefaction. Figure 4.21 shows the BET surface area plot between relative pressure \((P/P_0)\) and \(1/[Q(P_0/P-1)]\). The BET surface area was found to be 47.4277 m\(^2\)/g. The single point surface area at \(P/P = 0.280408876\) was found to be 46.8243 m\(^2\)/g.

4.4.7 FTIR Studies

Figure 4.22 FTIR absorption spectra of (a) raw alumina, and plasma synthesized powders obtained from (b) crucible, and (c) chamber of the reactor
Figure 4.22 shows the FTIR spectra of plasma synthesized product. The broad peaks at 677 and 1350 cm\(^{-1}\) are due to Al–N lattice stretching vibrations \([100]\) also confirming the presence of AlN in XRD and SAD pattern. The other peaks at 3417, 765, 974, 1600 and 1671 cm\(^{-1}\) are from impurities. Amorphous Al(OH)\(_3\) was observed in FTIR report of as-produced sample. The hydrolysis of sample might have been occurred in the FTIR studies as the samples were characterized long time after synthesis. The peaks at 3417 and 1600 cm\(^{-1}\) correspond to vibrational mode of O–H bond and physisorbed or weakly chemisorbed water \([252]\). The peak at 1671 and 974 cm\(^{-1}\) are vibrational and swing vibrational mode of O–H of Al(OH)\(_3\) \([253]\).

### 4.4.8 Raman Studies

![Raman spectrum](image)

Figure 4.23 Raman spectroscopy of (a) alumina and plasma synthesized nano powders obtained from (b) crucible and (c) chamber of the reactor

The Raman spectrum of the carbon free plasma synthesized product obtained from chamber wall, inner crucible and raw material alumina was shown in Figure 4.23. It is well known that the
space group of hexagonal AlN is $C_6^v$ (P63mc) with all atoms occupying the $C_{3v}$ sites. Six peaks centered at 248.64, 612.41, 655.81, 669.13, 897.2 and 906.91 cm$^{-1}$ are indexed to the first-order active vibrational Raman modes of $E_2$(low), $A_1$(TO), $E_2$(high), $E_1$(TO), $A_1$(LO) and $E_1$(LO) respectively [254], are observed. The observation is good agreement with that plasma synthesized product obtained from chamber is hexagonal AlN powder.

4.5 Synthesis of Aluminum Oxynitride (AlON) using plasma synthesized AlN powder

4.5.1 X-ray diffraction analysis

![XRD spectrum](image)

**Figure 4.24** XRD of plasma synthesized (a) powder of fused AlON; (b) fine AlN powder and (c) $\alpha$-$Al_2O_3$ powder
The XRD pattern the fused AlON is shown in Figure 4.24. All the peaks in the Figure 4.24 (a) are attributed to cubic $\gamma$-AlON with a lattice parameter of 7.910 Å which is good agreement with the standard value (7.937 Å, JCPDS Card No. 80-2173) [234]. No other peaks from impurities from AlN or $\text{Al}_2\text{O}_3$ are visible in the XRD pattern.

A single phase of AlON seems to form for the samples melted for 1 min, indicating that, once the sample melts, the reaction of AlON formation proceeds immediately. Thus, it should be noted that AlON has been successfully synthesized in 1 min by the plasma arc method, which is considerably faster than any other methods already reported.

4.5.2 Density

The density of the melted sample was measured following Archimedes principle was found to be 3.64 g/cc which is 98.11% of theoretical density. The theoretical density of AlON was reported to be of 3.71 g/cc.

4.5.3 Morphology and compositional study by Field Emission Scanning Electron Microscopy (FESEM) with EDAX and Electron Probe Micro Analysis (EPMA)

Figure 4.25 FESEM image of powder of fused AlON powder and its corresponding EDAX
Figure 4.26 EPMA micrograph with X-ray mapping showing the concentration of Al, N and O in AlON

Figure 4.25 shows the FE-SEM micrographs of the fragmented as-produced AlON spinel. It shows the formation of well faceted hexagonal shaped AlON spinel. EDS report confirms the presence of Al, O, and N at 1.5, 0.5 and 0.4 keV respectively in the plasma synthesized product and are found to be 46.39, 29.76 and 23.86 in atomic percentage respectively which is well consistent with the previously reported values [166]. The atomic percentage and weight percentage of all elements in the AlON are good agreement with the composition of AlON. Figure 4.26 shows the EPMA micrograph of Plasma melted AlON sample. This confirms the incorporation of Al, N and O element in the plasma synthesized melted sample.

4.5.4 Raman Analysis

Figure 4.27 shows the Raman spectra of plasma synthesized fused AlON. The spectrum composed of a number of phonon modes at 301.64, 395.77, 625.63, 748.93 and 913.52 cm$^{-1}$ in the range of 200 - 1200 cm$^{-1}$ which are good agreement with the previously published results [255].
4.5.5 FTIR Analysis

Figure 4.28 shows the FTIR spectra of plasma synthesized AlON sample. The peaks at 3449 and 1595 cm\(^{-1}\) are vibrational mode of O-H and the peak at 1386 cm\(^{-1}\) is swing vibrational mode of O-H. The peaks of 1357, 520 cm\(^{-1}\) correspond to AlN.

![FTIR spectrum of plasma synthesized AlON](image1)

Figure 4.27 Raman spectra of powder of plasma synthesized fused AlON

![Raman spectrum](image2)

Figure 4.28 FTIR spectroscopy of plasma melted AlON spinel
4.6 Sintering of plasma synthesized AlN powder

4.6.1 Density of the sintered AlN sample

The green densities of all samples were ~60% of the theoretical densities. Porosity decreased with the increase in sintering temperature and time. The density increases with the additive content. Figure 4.29 shows the variation of relative density with Y$_2$O$_3$ content sintered in thermal plasma for 15 min using N$_2$ and Ar as plasma forming gas. Theoretical density was estimated with the rule of mixtures. The relative density was calculated from the ratio of the bulk density and the theoretical density. It is confirmed that by adding 5 wt% Y$_2$O$_3$, AlN achieved 99.4 % of theoretical density.

During sintering, the liquid phase will attempt to occupy the lowest free energy position; thereby flowing to the smaller capillaries, which have the highest energy per unit volume. When there is insufficient liquid to fill all the pores, the liquid will attempt to pull the particles together to minimize the free energy. So the large increase in densification is attributed to the capillary forces exerted by the liquid phase on the solid particles. This effect gives rise to the rearrangement stage and rapid initial densification.

![Graph showing the dependence of relative density on Y$_2$O$_3$ content in the AlN sintered for 15 min.](image)

**Figure 4.29 Dependence of relative density on Y$_2$O$_3$ content in the AlN sintered for 15 min**
4.6.2 X-ray diffraction analysis

Figure 4.30 X-ray diffraction pattern of AlN sintered body with different wt% of $\text{Y}_2\text{O}_3$ showing AlN as the major crystalline phase, and $\text{Y}_3\text{Al}_5\text{O}_{12}$ (yttrium aluminium garnet) as the minor crystalline phase

Figure 4.30 shows the X-ray diffraction pattern of the sintered AlN body with different wt% of $\text{Y}_2\text{O}_3$ as sintering additive. It is observed that with the addition of $\text{Y}_2\text{O}_3$ to the AlN, there is no change in 2θ-value and peak intensity of AlN which imply that $\text{Y}_2\text{O}_3$ does not incorporate into the lattice of AlN. In all XRD pattern, the major crystalline phase was identified as AlN. However, with more addition of $\text{Y}_2\text{O}_3$, a secondary phase yttrium aluminium garnet ($\text{YAG} = \text{Y}_3\text{Al}_5\text{O}_{12}$ or $5\text{Al}_2\text{O}_33\text{Y}_2\text{O}_3$) is formed [256] which is visible in the XRD pattern of the sintered AlN (Figure 4.30). No other crystal phases were however identified. It is believed that while sintering, the oxygen inside the small crucible forms a thin layer of aluminium oxide on the surface of AlN powder, and that it reacts with $\text{Y}_2\text{O}_3$ to form a low melting point eutectic
phase. This phase is expected to be liquid at the sintering temperature, and gives rise to crystalline YAG on solidification. As a result, oxygen amount from AlN decreases which leads to increase in thermal conductivity of sintered AlN body [68].

4.6.3 Microstructure analysis

![Scanning electron microscope image of AlN sinter body with Y₂O₃ additive (a) 1, (b) 2, (c) 3, (d) 4 and (e) 5 wt%; (f) nano AlN sintered with 1wt% Y₂O₃ additive](image-url)
The grain and the grain boundary morphology vary with the $Y_2O_3$ content. Figure 4.31 shows the SEM images of the plasma sintered specimens with various $Y_2O_3$ additive (a) 1, (b) 2, (c) 3, (d) 4, (e) 5 wt% respectively. All these samples were sintered for 15 min. It is observed that the specimens shown in Figure 4.31 (a) and (b) are seen to be partial sintered and grain boundaries of the particles are sharp with small amount of secondary phase in the narrow grain boundary. It is observed that when $Y_2O_3$ wt% increase in the specimens, the sintered bodies became fully dense and no residual pores observed. However, with more $Y_2O_3$ content i.e. > 2wt% [Figure 4.31 (c) to (e)], the grain boundaries are seen to be less distinct rather than sharp edge. But secondary phases are not clearly visible. However, the distribution of secondary phases (white region) is seen to be more homogeneous and some grains are seen to be contiguous. The densification process of AlN ceramics was supported by liquid phase sintering while using sintering additives, accompanying solution-reprecipitation between AlN and the liquid phase which affected the final AlN densities. Figure 4.31 (f) shows the SEM micrograph of nano AlN sintered by adding 1wt% $Y_2O_3$ additive for 15 min in thermal plasma at load voltage-50 V and load current-300 A. The micrograph shows the plasma sintered nano AlN having high density with no pores. The EDAX spectrum of AlN sample with 5 wt% $Y_2O_3$ sintered for 15 min shown in Figure 4.32 which confirms the presence of oxygen impurities in the plasma sintered AlN is very less.

![Figure 4.32 EDAX of AlN sintered for 15 min with 5wt% $Y_2O_3$ sintering additive](image)

4.7 Fabrication of glass fiber reinforced epoxy hybrid composites filled with plasma synthesized AlN

4.7.1 Study of mechanical and physical properties of composites
4.7.1.1 Density of composites

Density of composites depends on the reinforcing materials, relative proportion of matrix. This is one of the most important factors determining the properties of the composites. The theoretical densities of samples were calculated based on the density of AlN, epoxy and glass fiber as 3.255, 1.15 and 2.590 g/cm$^3$ respectively as per the following equation;

$$\rho_{ct} = \frac{1}{\frac{W_f}{\rho_f} + \frac{W_m}{\rho_m} + \frac{W_p}{\rho_p}}$$

(4.14)

Where, $W$ and $\rho$ represent the weight fraction and density respectively. The suffix $f$, $m$, $ct$, $p$ stand for the fiber, matrix, composite materials and particulate filler materials respectively. The actual density $\rho_{ct}$ of the composite, however, can be determined experimentally by simple water-immersion technique. The volume fraction of voids $V_v$ in the composites was calculated using the following equation:

$$V_v = \frac{\rho_{ct} - \rho_{ce}}{\rho_{ct}}$$

(4.15)

Figure 4.33 Variation of density and void fraction in composites with different wt.% of plasma synthesized AlN powder
The theoretical and measured densities of the composites along with the corresponding volume fraction of voids are presented in Table 4.1.

Table 4.1 Density and void volume fraction of the PMCs filled with glass fiber and different wt. % of plasma synthesized AlN powder

<table>
<thead>
<tr>
<th>Composition</th>
<th>Measured Density (gm/cc)</th>
<th>Theoretical density (gm/cc)</th>
<th>Volume fraction of voids (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Epoxy</td>
<td>1.150</td>
<td>1.150</td>
<td>0</td>
</tr>
<tr>
<td>Epoxy+50 wt.% Glass fiber</td>
<td>1.535</td>
<td>1.544</td>
<td>0.56</td>
</tr>
<tr>
<td>Epoxy + 5 wt.% AlN + 50 wt.% Glass Fiber</td>
<td>1.591</td>
<td>1.619</td>
<td>1.75</td>
</tr>
<tr>
<td>Epoxy + 10 wt.% AlN + 50 wt.% Glass fiber</td>
<td>1.660</td>
<td>1.702</td>
<td>2.50</td>
</tr>
<tr>
<td>Epoxy + 15 wt.% AlN + 50 wt.% Glass fiber</td>
<td>1.733</td>
<td>1.794</td>
<td>3.50</td>
</tr>
</tbody>
</table>

It is clearly seen that with the incorporation of glass fiber in the neat epoxy creates the void fraction in the composite. With the addition of AlN as the filler material, more voids are found in the composites. As the filler content increases from 5 wt% to 15 wt%, the volume fraction of voids is found to be increase. The void content is the cause for the difference between the values of measured density and the theoretically calculated one. It has also been clearly seen in Figure 4.33 that with the increase in filler content, there is an increase in density. However, more addition of filler to matrix may create more voids which may affect on the mechanical, thermal and electrical properties of composites. The knowledge of void content is desirable for estimation of the quality of the composites. It is understandable that a good composite should have fewer voids. Higher void contents usually mean lower fatigue resistance, weathering and greater susceptibility to water penetration [257]. However, the presence of void is unavoidable in composite making particularly through hand-lay-up technique.
4.7.1.2 Micro-Hardness and Tensile strength of GFRE matrix

The variation micro-hardness and tensile strength of GFRE composites as a function of weight fraction of AlN particulates is given in Figure 4.34. It was observed that with the incorporation of filler particulates into the composites, the mean hardness improves significantly. Neat epoxy shows the average hardness of 13.7 HV. As the percentage of AlN increases, the hardness of composite increases significantly, 15 wt% of AlN-filled epoxy composite shows the maximum hardness of 35 HV.

![Figure 4.34 Variation of micro-hardness and Tensile Strength of GFRE Composites filled with different wt% of plasma synthesized AlN powder](image)

This may be attributed to the hard AlN particles getting pressed together with polymeric matrix phase and makes intimate contact with each other more tightly, as a result the interface can transfer load more effectively. Moreover, relatively uniform distribution of AlN particles and decrease in inter particle distance with increasing particle loading in the matrix results in increase of resistance to indentation of epoxy matrix. This can also be attributed to the surface coating AlN particles with a film of matrix which preventing the direct particle–particle contact.

It was observed that as the content of AlN particles increase, the tensile strength of composite decline gradually. There can be two reasons for this decline in the strength of these
particulate filled composites. One is that interfacial adhesion between AlN particles and the matrix may be too weak to transfer the tensile stress; the other is that the irregular shaped AlN particles act as stress raisers in the polymer matrix. Further it can be explained as follows: under the action of tensile force, the filler matrix interface is vulnerable to bonding, depending on interfacial bond strength and this may lead to a break in the composite.

4.7.1.3 Steady-state erosion behavior

Erosion behavior of the composites is generally ascertained by correlating erosion rate with impingement angle ($\alpha$), erodent velocity, and erodent particle size. Erosion behavior strongly depends on impingement angle. Figure 4.35 shows the influence of impingement angle on steady state erosion rate of epoxy and its composites.

Figure 4.35 Variation of erosion rate with impingement angle

It can be seen that filling of composite with AlN particles reduces the wear rate of the glass epoxy composite quite significantly. For the filled composites (with 5wt%, 10wt%, and 15wt% content) the value of $a_{\text{max}}$ is found to be 75°. In the present study, although the thermosetting polymer is ductile, the location of peak erosion has shifted to 60° from the usual
15°-30° as it is reinforced with glass fiber (curve A). This shift in the erosion behavior is an indication of loss of ductility and is obviously attributed to the brittle fibers. Further shifting of $\alpha_{\text{max}}$ from 60° to 75° (curve B, C and D) proves that the composites tend to become still more brittle with incorporation of AlN particles. The trend is similar for all the composites with AlN filler. Similar observation has been reported elsewhere [258]. Thus it can be concluded that erosion performance of glass epoxy composites improves with AlN filling and this improvement is a function of filler content within the limit of the present study.

4.7.1.3.1 Erosion mechanism

Material removal by impact erosion wear involves complex mechanisms. The erosion mechanism based on the assumption that the kinetic energy of the impinging particle is utilized to cause micro-indentation in the composite material and the material loss is a measure of indentation. The erosion is the result of cumulative damage of such non-interacting, single particle impacts. It is also assume that the erodent particles to be rigid, spherical bodied of diameter equal to the average grit size.

![Figure 4.36 Schematic of erosion mechanism in ductile mode](image)

It considers the ductile mode of erosion and assumes the volume of material lost in a single impact is less than the volume of indentation. The mechanism is based on the principle of
simplified approach of energy conservation, which equals the erodent kinetic energy with the work done in creating the indentation. However, the material removal during erosion is dependent on many material related factors and experimental conditions like hardness, size, volume fraction, arrangement of fibers, properties of matrix and interfacial bonding between fibers and matrix etc. The ductility mode of erosion proceeds as follows;

From the geometry of Figure 4.36, \( r^2 = d \times \delta \)

Where, \( r \) = chord length of indentation in meter, \( d \) = erodent diameter in meter and \( \delta \) = indentation depth.

The volume of indentation = \( \pi \delta^2 \left( \frac{d}{2} - \frac{\delta}{3} \right) \)  

(4.16)

So the volumetric wear loss per particle impact is given by

\[
e_v = \text{volume of indentation} \times \eta \quad \text{(Where } \eta \text{= erosion efficiency)}
\]

\[
= \eta \pi \delta^2 \left( \frac{d}{2} - \frac{\delta}{3} \right) \text{ and neglecting } \delta^3 \text{ term,}
\]

\[
= \frac{\pi d \delta^2}{2} \times \eta \quad \text{(4.17)}
\]

Considering \( N \) number of particle impacts per unit time, the volumetric erosion wear loss will be

\[
E_v = \frac{\pi d \delta^2}{2} N \times \eta \quad \text{(4.18)}
\]

Now applying conservation of energy to the single impact erosion process, kinetic energy associated with the normal velocity component of a single erodent particle is equal to the work done in the indentation of composite. The energy of impact introduces a force \( P \) on the indenter to cause the indentation in the composite. Thus,
\[ \frac{1}{2}mv^2\sin^2\alpha = \frac{1}{2}p\delta \]  \hspace{1cm} (4.19)

Where,

\( m \) = mass of single erodent particle, \( v \) = impact velocity and \( \alpha \) = angle of impingement.

\[ \text{So} \quad \frac{1}{2} \frac{\pi d^3}{6} \rho v^2\sin^2\alpha = \frac{1}{2} (\pi r^2 H_\nu) \delta \]  \hspace{1cm} (4.20)

Where,

\( H_\nu \) = Hardness (N/m^2) and \( \rho \) = density of erodent (kg/m^3)

On solving:

\[ \delta^2 = \frac{\rho v^2 d^2 \sin^2\alpha}{6H_\nu} \]  \hspace{1cm} (4.21)

The number of erodent particle impacting the target is estimated from the known value of erodent mass flow rate, \( M \) as

\[ N = \frac{M}{\pi d^3 \frac{\rho}{6}} \]  \hspace{1cm} (4.22)

Substituting the value of \( \delta \) in the Eq.(4.18)

\[ E_\nu = \frac{v^2 \sin 2\alpha}{2H_\nu} \cdot \eta \]

Erosion rate \( (E_\nu) \) defined as the ratio of mass lost due to erosion to the mass of erodent is now expressed as.

\[ E_i = \frac{\rho \cdot \eta v^2 \sin^2\alpha}{2H_\nu} \]  \hspace{1cm} (4.23)
### 4.7.1.3.2 Taguchi Analysis of the Erosion Test Results

#### Table 4.2 Signal to Noise ratio (S/N) and erosion rate for different test conditions

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
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<td>5</td>
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<td>2</td>
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<td>75</td>
<td>10</td>
<td>52.911</td>
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<td>3</td>
<td>33</td>
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<td>100</td>
<td>15</td>
<td>151.899</td>
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<td>4</td>
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<td>5</td>
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<td>60</td>
<td>100</td>
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<td>75</td>
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#### Table 4.3 Response for Signal to Noise Ratios

<table>
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<tr>
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<th>B</th>
<th>C</th>
<th>D</th>
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<td>2</td>
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<td>-54.05</td>
<td>-52.92</td>
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<td>Rank</td>
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<td>2</td>
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<td>4</td>
</tr>
</tbody>
</table>

The erosion wear rate of AlN filled glass epoxy matrix composites under various test conditions is given in Table 4.4. In Tables 4.4 the last columns represent S/N ratio of the erosion rate, which is in fact the average of three replications. The overall mean for the S/N ratio of the erosion rate is found to be - 49.15 db of AlN composites (Table 4.2). The analysis is made using the software specifically used for design of experiment applications known as MINITAB 14. The effects of individual control factors influencing the erosion wear rates of AlN filled glass epoxy composites are shown in Figure 4.37. Slope of each curve in the figure is a measure of the influence of that factor on the output. The S/N ratio response is also given in Table 4.3.
Table 4.4 Taguchi orthogonal array (L9) and erosion test results for AlN filled composites

From the figure and the table, it can be concluded that among all the factors, impact velocity is the most significant factor followed by AlN percentage and impingement angle, while the temperature has the least or almost no significance on erosion of the reinforced composite. It also leads to the conclusion that factor combination of A1, B3, C3, and D2 (Table 4.3) gives minimum erosion rate.

<table>
<thead>
<tr>
<th>(A) Velocity (m/s)</th>
<th>(B) Impingement Angle (θ)</th>
<th>(C) Temp. (°C)</th>
<th>(D) Filler (%)</th>
<th>Pressure (bar)</th>
<th>Initial weight (gm)</th>
<th>Final weight (gm)</th>
<th>Difference (gm)</th>
<th>Erosion rate (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>50</td>
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<td>15</td>
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<td>10</td>
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<td>0.05163</td>
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</table>

Figure 4.37 Effect of control factors on erosion rate (AlN filled composites)
4.7.2 Study of morphology of composites

4.7.2.1 Surface Morphology of eroded samples

The surface microstructure of the eroded composite samples is observed under FESEM Zeiss, Supra-55. The morphologies of eroded surfaces were studied to identify the mode of material removed. Figure 4.38 (a) & (b) represents the microstructure of the composite eroded at high impact velocity (47 m/s and 57 m/s) and at an impingement angle of 60° and 30°.

Figure 4.38 FESEM photomicrograph of eroded (a) 10% AlN filled glass - epoxy composite (60° Impingement angle and 75°C temp.) (b) 5% AlN filled glass - epoxy composite (30° Impingement angle and 50°C temp.) (c) & (d) 5% AlN filled glass - epoxy composite (30° Impingement angle and 50°C temp.) surface

It shows local removal of epoxy material from the impacted surface resulting in exposure of the fibers to the erodent flux. The formation of transverse crack in the composite material is
mainly due to particle impact on fiber which is clearly visible in SEM micrograph. The propagation of crack along transverse as well as longitudinal direction is well visualized. It is obvious from Figure 4.38 (a) that the fibers are completely broken by means of shearing action and protruding of fibers from matrix is due to impingement of alumina particles at higher impact velocity. At higher impact velocity, continuous exposure of fibers to erosion environment results in fiber thinning and detachment of fibers from matrix. Cavities left after fiber being dislodged are also seen. Similar observation was observed in literature [259]. Figure 4.38 (c) shows the microstructure of the AlN-filled composite eroded with high-impact velocity (57 m/s) at an impingement angle of 30°. It shows local removal of resin material from the impacted surface resulting in exposure of the fibers to the erodent flux. This micrograph Figure 4.38 (d) also reveals that due to particle impact on glass-fibers, there is formation of transverse cracks that break these fibers. The propagation of crack along transverse as well as longitudinal direction is well visualized. It appears that cracks have grown on the fibers giving rise to breaking of the fibers into small fragments. Further the cracks have been annihilated at the fiber matrix interface and seem not to have penetrated through the matrix. Figure 4.38 (d) also shows the dominance of micro-chipping and micro-cracking phenomena. From Figure 4.38 (b), it can be seen that multiple cracks originate from the point of impact, intersect one another and form wear debris due to brittle fracture in the fiber body as well as in the AlN particles present in the epoxy body. After repetitive impacts, the debris in platelet form is removed and account for the measured wear loss.

4.7.2.2 Surface morphology of Tensile Fractured Composites

Figure 4.39 (a), (b), (c) and (d) shows the morphology of the tensile fractured GFRE matrix composite with 0, 5, 10 and 15 wt% plasma synthesized AlN powder respectively. It is evident from Figure 4.39 (a) that the layers of polymer and bidirectional glass fiber staked one over another and fairly bonding with each other. Lateral view of the tensile fractured glass fiber can be observed in Figure 4.39 (a) and (b). It is evident that glass fibers are well embedded in epoxy which improves the mechanical properties of the composites. There is no observation of AlN particles in the micrograph of GFRE composite filled with 5 wt% of AlN because of low filler concentration and well dispersion of the filler particles in epoxy. As the concentration of
AlN increases up to 10 wt%, the formation of voids started (shown in Figure 4.39 (c)) which affects the mechanical, electrical as well as Thermal properties of the composites. In 15 wt% of the AlN loading, agglomeration/clusters of AlN particles were forms inside composite which is shown in Figure 4.39 (d). There is no observation of particle-matrix debonding, micro cracks on the surface of composites which suggesting the relatively strong interfacial bonding and good compatibility of AlN particles with the epoxy matrix. This further corroborates the enhancement of thermal conductivity, mechanical and electrical property of GFRE matrix with AlN filler.

Figure 4.39 Microstructure of tensile fractured GFRE composites with (a) 0, (b) 5, (c) 10 and (d) 15 wt% of plasma synthesized AlN powder

4.7.3 Study of thermal properties of composites

4.7.3.1 Thermal Conductivity, Glass Transition Temperature \( (T_g) \) and Thermal Stability

The thermal conductivity values of GFRE composite are shown in Figure 4.40 (a). It shows, with the inclusion of plasma synthesized AlN filler in GFRE composites, the thermal conductivity value increases significantly. At 5 wt% of AlN filler loading, the thermal conductivity of GFRP composite shows 0.241 W/mK and it increases to 0.300 W/mK at 10 wt%
of loading which is 2.11 times of neat epoxy and it subsequently increases to 0.322 W/mK with 15 wt% of AlN loading which is 2.25 times of neat epoxy.

![Diagram](image)

**Figure 4.40** Variation of (a) Thermal conductivity and (b) flow of heat in PMC filled with glass fiber and different wt% of plasma synthesized AlN powder

The filler particles at low volume fraction can disperse randomly in the epoxy matrix and has weak interaction each other to present a little increase of thermal conductivity. As the filler loading increases the particles begin to touch each other, and to form partial conductive path or network which enhance heat conductance. Thermal conductivity of glass fiber is larger than the epoxy [260].

The direction and length of glass fiber also make a continuous path for phonons to transfer heat. Hence reinforcement of glass fiber not only increases mechanical properties but
thermal conductivity too. The DSC curves of neat epoxy, glass fiber reinforced epoxy composite and GFRE matrix with different wt % AlN filler (5, 10 and 15 wt%) composites are plotted in Figure 4.40 (b). The thermogram shows the endothermic glass transition temperature of neat epoxy at 66.53°C. It can be observed that reinforcement of glass fiber and AlN powder in to epoxy does not seem to have appreciable influence on the $T_g$. However, at 15 wt% AlN loading, $T_g$ reduced to 64.8°C. The decrease in $T_g$ may be due to the decrease in polymer matrix interaction and formation of agglomeration of AlN particles in the composites [261]. The agglomeration or cluster formation occurs at higher filler loading which is visible in SEM micrograph (Figure 4.39 d) of composites.

![Image of TGA curves](image)

**Figure 4.41 TGA curves of neat Epoxy and GFRE composites filled with different wt% of plasma synthesized AlN powder**

The TGA curves of GFRP composites are shown in Figure 4.41. It is obvious from graph that the thermal stability of GFRP composites increases with increasing AlN concentration. The reason may be ascribed to the higher heat capacity $0.738 \text{ Jg}^{-1} \text{°C}^{-1}$ of AlN, as compared to epoxy resin and high thermal conductivity of 170 W/mK, compared to 0.142 W/mK of neat epoxy. The
inclusion of high thermal conductive AlN and glass fiber in epoxy, cause it to preferably absorb the heat. So, this will result in epoxy chains starting to degrade at higher temperature.

4.7.4 Study of electrical properties of composites

4.7.4.1 Dielectric Breakdown Strength

Dielectric breakdown strength is defined as the highest voltage which samples can stand before they fail electrically, divided by sample thickness. Breakdown of polymer dielectrics depends on many factors such as degree of crystallinity, accumulation of bulk charge, interfacial area, temperature, types of bonding and free volume [262]. Figure 4.42 shows the AC dielectric break down strength of neat epoxy and GFRE composites at variable AlN loading.

![Graph of Dielectric Strength vs Specimen](image)

Figure 4.42 Variation of dielectric breakdown strength of PMC filled with glass fiber and different wt% of plasma synthesized AlN powder

It is evident that break down strength of neat epoxy varies accordingly with the reinforcement of glass fiber and AlN powder. At 50 wt% of glass fiber loading breakdown strength increases marginally the up to 20.55 kV whereas neat epoxy shows only 11.88 kV. However, at filler concentration of 5 wt%, the break down strength of the composite remains almost the same as the GFRE composite.
This behavior is probably because at lower concentration of filler, the number of AlN particles is less, the inter particle distances are more and the volume fraction of the loose polymer layer is large under the condition of high electric stress, a large fraction of those polymer layer allow the transfer of charge carrier between the electrodes thereby loading to lower or marginally same breakdown voltage as the epoxy [39]. At 10 wt% of AlN loading, the composite shows maximum dielectric breakdown strength of 30.26 kV. The reason may be due to high packing density, the accumulated charge is reduced and reduced threshold field at any point and alteration of space charge distribution [263]. The bonding between filler particles and epoxy matrix would lead to form denser structure which might limit the mobility of matrix backbone which leads to increase in the dielectric breakdown strength [264]. Again the number of particles in the composite is larger with the inter particle distance being smaller, hence the volume fraction of loose polymer layer reduces and the particles themselves act as barriers to flow of current between the electrodes. These factors contribute to oppose in the flow of current in the composite, resulting in higher breakdown voltage [39]. At higher filler content i.e. 15 wt% of AlN loading, the dielectric breakdown strength again decreases marginally to 22.34 kV. This effect may be attributed to the formation of agglomeration of fine AlN particles in the GFRE composites resulting the defects such as voids [265].

4.7.4.2 Volume Resistivity

Figure 4.43 shows the variation in the DC volume resistivity of neat epoxy and GFRE composites at variable wt% of AlN filler. Neat epoxy shows a resistivity value of $3.31 \times 10^{15}$ $\Omega \cdot \text{cm}$ which decreases with the incorporation of glass fiber and plasma synthesized fine AlN powder. As glass fiber sheets were layer wise sandwiched in epoxy, it doesn’t significantly affects on the volume resistivity as the conduction path through the epoxy is obstructed by laminated glass fiber sheets result small increase in volume resistivity [266]. With 50 wt% of glass fiber reinforcement in neat epoxy shows the volume resistivity value of $8.51 \times 10^{15}$ $\Omega \cdot \text{cm}$. However, with 5 wt% incorporation of plasma synthesized fine AlN particles to the GFRE reduces significantly the resistivity value to $3.01 \times 10^{14}$ $\Omega \cdot \text{cm}$. This behavior indicates that at lower filler loading, the fraction of extended loose polymer and glass fiber layers is high which probably allows the existence of free ions and also their unhindered transport through the bulk of
the material those results in an increase in the electrical conductivity through the volume of the material. However, with the increase in AlN loading up to 10 wt%, immobilized polymer chains act as ion traps which inhibit the ion mobility which opposes the flow of electrons thereby resulting in decrease in the overall conductivity values i.e. increase in volume resistivity [39].

Further, incorporation of AlN (i.e. at 15 wt%) leads to the reduction in volume resistivity as filler makes partial interconnections between the particles lead to the margin decrease of volume resistivity of GFRE composite system. Similar type of observation was observed in a previously reported paper related to the influence volume resistivity of epoxy/nano alumina composites on the filler percentage [267].
4.8 Fabrication of LLDPE/AlN composites and study of its thermal and mechanical properties

4.8.1 Study of mechanical and physical properties of composites

The tensile properties of LLDPE and its composites at various AlN contents are shown in Figure 4.44.

![Figure 4.44 Effect of AlN weight fraction on tensile strength of LLDPE/AlN composites](image)

It shows the effects of AlN mass fraction on the tensile strength of AlN/LLDPE composites. The tensile strength of AlN/LLDPE composites increases up to 30 wt% of AlN loading, but it may decrease with the excessive addition of AlN [268]. For given AlN loading and PUCA modification of AlN resulted in AlN/LLDPE composites with enhanced tensile strength of composites. The modification of AlN enhances the adhesion strength of interface, thus to improve the tensile strength of composites. The effect of filler on tensile strength may be due to the counterbalance of two reasons; with the increase in the filler content in a polymer composite there is increase in effective surface fracture energy, size of voids and agglomeration of filler
particles. The dispersed particles make the crack propagation path longer, absorb a portion of energy and enhance the plastic deformation. Therefore, the surface fracture energy increases and the strength of composites increase with volume percentage of filler. However, with increase in mica content, the size of voids formed when the polymer matrix detaches from the filler particles became critically large and initiates the main crack [269]. The results are attributed to the oriented structure of AlN, which can reduce defects, transfer stress, and prevent the expanding of crazing inside the LLDPE matrix. Tensile modulus of LLDPE filled with plasma synthesized AlN composites increased rapidly with the content of filler as shown in Figure 4.45. The tensile modulus increases with incorporation of filler in the polymer matrix. The increase in the tensile modulus of LLDPE/AlN composite is due to the increase in the crystallinity of composites by addition of AlN. The variation in the rate of change of increase in tensile modulus indicates that effect of intermolecular interaction of matrix and filler.

![Figure 4.45 Effect of AlN fraction on the tensile modulus of LLDPE/AlN composites](image)

Elongation at break of LLDPE filled with plasma synthesized AlN filler composites decreased with increase in filler content as shown in Figure 4.46. It can be observed that pure LLDPE has
higher values of elongation at break, as compared to its AlN composites. Reinforcement of AlN filler introduces discontinuity in stress transfer to the filler-polymer interface in the composites structure. When external force is applied, the LLDPE chains have enough space and time to orientate, which is the result of the chemical structure of LLDPE, when the chains are orientated, they start to form orientation crystallinity, which evokes an increase in the strength of a LLDPE sample. Incorporating AlN particles to the LLDPE matrix reduces chains mobility which leads to a rapidly decreasing elongation at break [227]. The rate of decrease in elongation at break of composites shows that the brittleness of composite increases with the AlN content. The AlN particles give the reinforcement effect due to its heterogeneous structure. Such a significant drop could be due to the agglomeration of AlN which acts as the crack initiation.

![Graph](image)

**Figure 4.46 Effect of AlN fractions on the elongation at break of AlN/LLDPE composites**

Charpy impact test is a high speed fracture test that measures the energy to break the specimen under banding condition. The specimen is deformed within a short time and therefore exposed to high strain. The reinforcement seems to be very effective up to 10 wt% of AlN since
there is a little decrease in Charpy impact strength. The impact strength had a sudden drop after 10 wt % of AlN as shown in Figure 4.47. From the figure it can be noted that the Charpy impact strength of all composites of LLDPE/AlN are lower than that of virgin LLDPE. AlN leads to easy crack initiation along with more brittle nature of composites. The increase in toughness may be caused by the inhomogeneous particle shape and size of micro particles. Since the edges of AlN particles have different angularities and they would facilitate failure under impact condition due to localized stress concentrations.

![Charpy impact strength vs. Wt % of AlN](image)

**Figure 4.47 Effect of AlN fraction on the impact strength of the LLDPE/AlN composites**

4.8.2 Study of Thermal properties of composites

4.8.2.1 Melting temperature and degree of crystallinity

The DSC curves of native LLDPE and its AlN composites are plotted in Figure 4.48. It can be observed that the AlN content does not seem to have appreciable influence on the melting temperature of LLDPE, and the peak temperature of melting ($T_m$) very slightly shifts toward a lower temperature with increasing AlN loading. The reason may be that the AlN filler probably reduces of lamellar thickness of crystallites and thus it leads to a decrease of melting temperature
[227], because some AlN particles will fill themselves in the interlamellar space due to a higher degree of crystallinity of pure LLDPE.

Figure 4.48 DSC melting curves of LLDPE and LLDPE/AlN composites

With increasing AlN content the degree of crystallinity \( (X_v) \) of LLDPE decreases as compared to native LLDPE. The reason may be that the LLDPE has a relative high crystallinity, and has not a major amorphous part in which the AlN particles can be accommodated. At low filler loading the filler particles locate themselves in the interlamellar space, which leave little space for additional crystallization, and the presence of filler may even inhibit crystallization. At high filler content there is probably a change in crystallization mechanism [227]. It is therefore possible for the fillers to decrease the mobility of LLDPE chains in the formation of crystallites and, as a result, the domains of crystalline phase are reduced in size [270]. It is also likely that imperfection of crystals in the presence of the AlN inhomogeneities contributes to the decrease in crystallinity [270].

\[
X_v = \frac{(H_m - H_c) \rho_c}{H_f (1 - X_{ms}) \rho_c -(H_m - H_c)(\rho_c - \rho_a)}
\]  
(4.24)
Where,

\( X_v = \) Volume fraction crystallinity.

\( H_m = \) heat of fusion measured as the area of melting peak.

\( H_c = \) heat of additional crystallization measured as the area under the crystallization peak.

\( H_f = \) theoretical heat of fusion for a pure crystalline phase for LLDPE.

\( \rho_a = \) density of amorphous phase for LLDPE.

\( \rho_c = \) density of crystalline phase for LLDPE.

\( X_{ms} = \) mass fraction of reinforcement.

### 4.8.2.2 Thermal Conductivity and Thermal Stability

![Figure 4.49 Variation of thermal conductivity with AlN wt%](image.png)

The thermal conductivity values of AlN/LLDPE are shown in **Figure 4.49**, as can be seen that they increase obviously with an increase in filler loading. The filler particles at low volume fraction can disperse randomly in the LLDPE matrix and have weak interaction each other to present a little increase of thermal conductivity. As the filler loading increases the particles begin to touch each other, and to form partial conductive path or network which enhance heat
conductance. At 30 vol% AlN content, the thermal conductivity reached up to 0.417 W/m.K, which is 1.8 times that of pure LLDPE. Figure 4.49 suggests that the use of titanate coupling agent during the melt mixing is to functionalize the surface of AlN obviously improved the thermal conductivity compared to the untreated filler reinforced LLDPE at AlN content. It is well known that the transport of heat in all non-metals is by the flow of lattice vibration energy [216], or phonons, along the temperature gradient within the specimen; for a two phase system like AlN/LLDPE composites, interfacial physical contact between polymer and filler is very critical, since phonons are very sensitive to surface defects [271]. Thermal resistance is caused by various types of phonon scattering processes, and the interfacial thermal barriers in composites is mainly due to the scattering of phonons resulting from acoustic mismatch and flaw associated with the matrix–filler interface [272]. The interface between the two-phase composites acts as a barrier of heat transmission. So, the addition of PUCA titanate coupling agent improves the interfacial bonding between AlN and matrix, and reduces the voids at the filler–matrix interface, which facilitates enhancing the thermal conductivity.

![Figure 4.50 Thermal conductivity of LLDPE/AlN composites as a function of temperature](image-url)
Chapter IV

Results and Discussion

The influence of temperature on the thermal conductivity of composites for different AlN filler content is presented in Figure 4.50. It is noticed that the thermal conductivity of the composites decreases slightly as temperature increases within the testing temperature range. The reason for the decrease might be that the volume of composites expands slightly when heated, and the distance of adjacent conductive filler particles increases slightly, thus leading to a decreased thermal conductivity.

![Figure 4.51 Thermogravimetric analysis of LLDPE filled with different wt% of plasma synthesized AlN](image)

The TGA curves for AlN/LLDPE composites are illustrated in Figure 4.51. There is an obvious increase in the thermal stability of LLDPE with increasing AlN concentration. The reason may be ascribed to the higher heat capacity $0.738 \text{ Jg}^{-1}\text{C}^{-1}$ of AlN, as compared to $0.18 \text{ Jg}^{-1}\text{C}^{-1}$ of LLDPE and the high thermal conductivity of 170 W/m K, compared to 0.264 W/m.K of native LLPDE, which will cause it to preferably absorb the heat. So, this will result in LLDPE chains starting to degrade at higher temperature [227].

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4.8.2.3 Dynamic Mechanical Analysis (DMA)

Figure 4.52 shows the storage modulus attained, as a function of the temperature for the various LLDPE systems. The figure shows that the storage modulus of neat LLDPE and LLDPE composites with 10, 20, and 30 wt% AlN filler are 2974.29, 3965.72, 4430.37, 4691.22 MPa respectively. In the glassy state the incorporation of plasma synthesized aluminium nitride (AlN) yielded a 57.72% increase in storage modulus as compared to virgin LLDPE. This enhancement in storage modulus may be due to the decrease in crystallinity and enhancement of free volume on increase of AlN content in the LLDPE matrix resulting in the stiffness and sufficient energy storage in the material [273]. It can be definitely considered that the homogeneous dispersion and the excellent interfacial coupling force in a mixture state of the micro particles limits the mobility of the LLDPE molecules and enhance the storage modulus.

![Figure 4.52 Storage modulus versus temperature of LLDPE and composites filled with different weight percentage of plasma synthesized AlN powder](image-url)
The variation of loss tangent with temperature for pure LLDPE and their blends at different composition are shown in Figure 4.53. Pure LLDPE, due to its molecular structure and high crystallinity, shows three different relaxation peaks, namely α, β and γ over the temperature range −150 °C to +150 °C [273].

![Image of graph showing loss modulus versus temperature for different compositions of AlN powder in LLDPE](image)

**Figure 4.53 Loss modulus versus temperature of LLDPE and composites filled with different weight percentage of plasma synthesized AlN powder**

However, in Figure 4.53, the α-relaxation at 58.62 °C is not clearly observable which is associated with the vibrational and re-orientational motion of −CH₂− sequences with in the crystal [274]. The β-relaxation observed at ~ 0 °C is associated with the side branching of LLDPE. The γ-relaxation occurring at lowest temperature (~118.58 °C) is associated with the movement of methylene unit both in the amorphous and crystalline phase of the polymer. This is also considered as the glass rubber relaxation of the poly methylene group, which is the main backbone of LLDPE [275]. It is seen that by increasing AlN content all α, β and γ transition
peak temperatures shift to a lower temperatures in the blend. These decreases in $\alpha$-transition temperature are probably due to the plasticization effect of the AlN content, which decreases the crystallinity of LLDPE phase by enhancing the molecular motion, leading to a lower $T_g$.

**Figure 4.54** shows Tan δ versus temperature of LLDPE and composites filled with different weight percentage of plasma synthesized AlN powder. The temperature corresponding to the tan δ peak shifts slightly toward higher temperature with increase in AlN proportion.

![Figure 4.54 Tan δ versus temperature of LLDPE and composites filled with different weight percentage of plasma synthesized AlN powder](image)

**4.8.2.4 Morphology of tensile fractured surface of LLDPE/AlN composites**

The micro-structure images of LLDPE filled with 10, 20 and 30 wt% of plasma synthesized filler are depicted in **Figure 4.55 (a), (b) and (c)** respectively. The AlN powder distributions are found to be relatively rather uniform. It is observed that, the LLDPE are surrounded with AlN particles though there is some connectivity between adjacent LLDPE particles in small regions and to a certain degree, thermal conductive channels can be easily
formed in the composites. **In Figure 4.55 (c), it is observed that some particle clusters are formed.** At high filler loading the most of adjacent AlN particles could touch each other, and form particles clusters or partial conductive pathways in composites. The thermal resistance is therefore reduced owing to the connectivity of some filler particles, leading to a high thermal conductivity.

![Figure 4.55 SEM image of LLDPE filled with (a) 10 wt%, (b) 20 wt% and (c) 30 wt% of plasma synthesized AlN powder](image)

Figure 4.55 SEM image of LLDPE filled with (a) 10 wt%, (b) 20 wt% and (c) 30 wt% of plasma synthesized AlN powder