CHAPTER 9

SUMMARY AND CONCLUSION

The aim of the present work is to develop and characterize organic-inorganic hybrid polymer nanocomposites by using three different reinforcements like amine terminated cyclophosphazene, functionalized rice husk ash and functionalized TiO$_2$ nanoparticles. The above inorganic materials were incorporated with various types of organic matrices such as epoxy, cyanate ester, benzoxazine, bismaleimide and caprolactam. The hybrid composites were characterised by different characterization techniques to ascertain their utility for high performance applications. The resultant organic-inorganic hybrids have improved thermal, dielectric, hydrophobic, mechanical, flame retardant, antibacterial and corrosion resistant properties.

Chapter 1 reviews the introductory part of the polymer nanocomposites, organic-inorganic hybrid nanocomposites, cyanate ester, epoxy, benzoxazine, bismaleimide, caprolactam, cyclotriphosphazene, rice husk ash, and titanium dioxides including the literature review were discussed. Chapter 2 describes the material details, reinforcement synthesis and preparation procedure adopted for the synthesis of hybrid materials.

A new flame retardant amine terminated cyclophosphazene and silane functionalized rice husk ash based epoxy (ATCP/FRHA/Ep) composites have been developed and their properties like thermal stability, flame retardancy, dielectric behaviour and hydrophobic nature were evaluated in Chapter 3. The SEM images exhibit the smooth fracture surface of
ATCP/FRHA/Ep composites and the nonphase separated homogeneous morphology owing to the chemical linkage among the amine terminated cyclophosphazene, functionalized rice husk ash materials and epoxy resin. The XRD analysis indicates the amorphous nature of synthesized materials. The values of dielectric constant and dielectric loss of ATCP/FRHA/Ep composites have found to be decreased when the concentration of rice husk ash increased, which is due to its insignificant polarizability. The nyquist plots concluded that the increase in electrical resistivity are observed with an increase in wt.% of functionalized rice husk ash into the amine terminated cyclophosphazene based epoxy composites. Water absorption analysis and contact angle measurements (CA) conclude that the hydrophobic nature of ATCP/FRHA/Ep has been improved due to presence of inorganic segments.

Data obtained from TGA and DSC analysis infer that the presence of amine terminated cyclophosphazene and functionalized rice husk ash could improve the thermal stability, char yield and glass transition temperature. Analysis from cone calorimeter test provides the information about the flame retardant behaviour such as HRR, THR, COP, SPR and TSP. The presence of phosphorous, nitrogen and silica in the epoxy composites can influence the flame retardant properties with respect to their percentage concentration. The data obtained from different studies indicate that the amine terminated cyclophosphazene and silane functionalized rice husk ash based epoxy (ATCP/FRHA/Ep) composites can be used as better flame resistant material in the place of conventional epoxy matrix for enhanced performance and improved longevity.

In **Chapter 4**, amine terminated cyclophosphazene and functionalized rice husk ash were utilized together as a novel combined halogen free flame retardant system to improve the flame retardance of benzoxazine blended epoxy composites. The addition of FRHA enhances both
flame retardance and dielectric properties of amine terminated cyclophosphazene reinforced benzoxazine based epoxy matrix. The fractured surfaces exhibit a non-phase separated platelet like homogeneous morphology. The dielectric constant and loss were decreased due to the presence of intramolecular hydrogen bonding, high cross linking density and orientation of the molecule. The improvement in the electrical resistivity was confirmed by Nyquist plot. The enhanced hydrophobic nature was confirmed by contact angle measurements. Further, the introduction of small amount of ATCP and FRHA were accelerated to improve the degradation properties, which are due to a compact and unbroken N, P and Si protective layer. Therefore, drastically depressed peak heat release rates were achieved. This novel flame retardant composite will pave a new possibility for high performance halogen free flame retardant polymeric materials, which could be applied for micro-electronic devices.

The high cross linked ATCP/CE hybrid composites were prepared and their molecular structures were ascertained from FT-IR, $^1$H-NMR, $^{13}$C-NMR, and $^{31}$P-NMR analysis. An incorporation of 5 wt.%, 10 wt.% and 15 wt.% CPA in to CE matrix system improves the values of $T_g$ and thermal stability with enhanced char yield. SEM analysis exhibits homogeneous morphology due to perfect bonding between CE and ATCP through imino carbonyl adducts formation and highly cross linked polymerization. The values of dielectric constant and dielectric loss were found to be decreased with increasing the concentration of ATCP due to its insignificant polarizability. Data resulted from different studies indicate that ATCP (15%)/CE hybrid materials can find application in the field of microelectronic applications for better performance than neat cyanate esters and other ratios of ATCP incorporated CE composites.
Further, amine terminated cyclophosphazene and functionalized rice husk ash incorporated cyanate ester blended epoxy (ATCP/FRHA/CE-Ep) composites have been developed and their properties like thermal stability, flame retardancy, dielectric behaviour and hydrophobic nature were evaluated in Chapter 5. The values of dielectric constant and dielectric loss for ATCP/FRHA/CE-Ep composites have found to be decreased when the concentration of rice husk ash is increased due to its insignificant polarizability. The Nyquist plots infer that there is an increase in electrical resistivity with an increase in wt.% of functionalized rice husk ash into the amine terminated cyclophosphazene reinforced cyanate ester based epoxy composites. Water absorption analysis and contact angle measurements (CA) show the improved hydrophobic nature for ATCP/FRHA/CE-Ep composite due to presence of inorganic segments. Data obtained from TGA and DSC analysis infer that the presence of amine terminated cyclophosphazene and functionalized rice husk ash in the CE-Ep composite could improve their thermal stability, char yield and glass transition temperature. Analysis of cone calorimeter test provides the information about the flame retardant behaviour such as HRR, THR, COP, SPR and TSP. From the results it has been concluded that ATCP(15%)/FRHA(5%)/CE-Ep composites possess enhanced thermal, electric resistance, hydrophobicity and flame retardant properties when compared with other ratios of FRHA incorporated ATCP(15%)/CE-Ep composites. Hence, the amine terminated cyclophosphazene and functionalized rice husk ash incorporated cyanate ester blended epoxy (ATCP (15%)/FRHA(5%)/CE-Ep) composites can be used as better flame resistant material in the place of conventional epoxy matrix for enhanced performance and improved longevity.

The ATCP/FRHA/CE-Ep composites possess better performance with regards to flame retardant, thermal, hydrophobicity, dielectric and morphologies than those of ATCP/FRHA/Ep and ATCP/FRHA/Bz-Ep
composites. This is due to presence of high performance thermosetting cyanate ester resin, which has outstanding flame retardant, mechanical, dielectric and thermal stability compared to other polymer matrix.

Chapter 6 explains the cyclophosphazene incorporated benzoxazine and bismaleimide blended (ATCP/Bz-Bmi) composites were obtained through ring opening polymerization with benzoxazine and bismaleimide polymerized via Michal addition with phosphazene group and Diels-Alder reaction with polybenzoxazine group by solution polymerization via thermal cure method. The resulting (5, 10 and 15%) ATCP/Bz-Bmi composite acquired enhanced thermal, dielectric and significant mechanical performance than those of pristine Bz-Bmi composite, which is due to the presence of imide linkage between phosphazene group and the bismaleimide skeleton. The fractured surfaces are rough and irregular in appearance are noticed in the case of ATCP loaded Bz-Bmi system, which demonstrates good compatibility between the polymer matrix and ATCP phase. This may be due to the chemical interaction, good miscibility and compatibility between polymer matrix and phosphazene. The antibacterial properties of ATCP/Bz-Bmi composites exhibit better perform against *S. aureus* and *E. coli* bacteria. Such properties could be utilized to inhibit the bacteria growth for further use in microelectronic applications. Data obtained from different studies indicate that the ATCP(15%)/Bz-Bmi composites developed in the present study can be used as potential candidate for high performance applications.

Amine terminated cyclophosphazene (ATCP) and functionalized TiO$_2$ nanoparticle incorporated cyanate ester (CE) based caprolactam (Cpl) nanocomposites (ATCP/FTiO$_2$/CE-Cpl) coatings were successfully prepared on mild steel through a dip coating followed by thermal cure method (Chapter 7). The corrosion protection ability of CE-Cpl, ATCP/CE-Cpl and
ATCP/FTiO₂/CE-Cpl were investigated by open circuit potentials, Tafel curve and EIS graphs.

The results showed that the protection efficiency of ATCP/CE-Cpl is higher than those of CE-Cpl composites and bare MS plate. From the above system it has been noticed that ATCP(15%)/CE-Cpl composite has higher corrosion resistance when compared with those of other ratios of ATCP incorporated CE-Cpl composites. In addition to that the various percentages of FTiO₂ incorporated ATCP(15%)/CE-Cpl composites coated MS plates have more corrosion resistance properties (more than 97%) when compared with that of ATCP(15%)/CE-Cpl composites. From the results, it has been concluded that ATCP/FTiO₂/CE-Cpl composite coatings material exhibit higher corrosion prevention on MS plates.

Chapter 8 explains the amine terminated cyclophosphazene (ATCP) and functionalized TiO₂ nanoparticle incorporated benzoxazine (Bz) based cyanate ester (CE) nanocomposites (ATCP/FTiO₂/Bz-CE) coatings were successfully prepared on mild steel through a dip coating followed by thermal cure method. The structure has been confirmed by FT-IR and surface morphologies of the nanocomposites were studied by using FESEM, HRTEM and XRD analysis. The corrosion protection ability of ATCP/FTiO₂/Bz-CE has been investigated by open circuit potentials, Tafel curve and EIS graphs. The results conclude that the protection efficiencies of all ATCP/FTiO₂/Bz-CE composites coated MS plates are more than 99%. From the results, ATCP/FTiO₂/Bz-CE composites as coatings material can attract commercial application for the prevention of corrosion on MS plate.

ATCP/FTiO₂/Bz-CE nanocomposites possess better corrosion resistance properties than that of ATCP/FTiO₂/CE-Cpl nanocomposites. ATCP/FTiO₂/Bz-CE composite exhibits 99% corrosion resistance in Tafel fit curves. The antibacterial properties of ATCP/FTiO₂/Bz-CE nanocomposites
shows higher activity compared to ATCP/FTiO$_2$/CE-Cpl nanocomposites, which is due to the presence of polybenzoxazine in the nanocomposites. Since caprolactam is a thermoplastic material and benzoxazine is a thermosetting material, ATCP/FTiO$_2$/Bz-CE has higher thermal properties than ATCP/FTiO$_2$/CE-Cpl nanocomposites.

Data resulted from different studies such as thermal, flame retardant, mechanical, corrosion resistance, hydrophobicity, antibacterial, dielectric and morphological properties indicate that the incorporation of amine terminated cyclophosphazene into epoxy, cyanate ester, benzoxazine, bismaleimide and caprolactam based composites possess better characteristic properties than those of other matrices. Other inorganic reinforcements like functionalized rice husk ash and functionalized titanium dioxide also play a vital role along with amine terminated cyclophosphazene to improve polymer matrix properties. Hence, amine terminated cyclophosphazene, rice husk ash and titanium dioxide incorporated hybrid nanocomposites can be used in the form of adhesives, sealants, coatings, matrices and advanced composite materials for engineering and marine applications under severe and harsh environments with improved longevity.

Further, the present work may be extended in the future to improve the flame retardant and dielectric properties of thermosetting polymer by using nano sized phosphazene based sulphone fiber reinforced carbon nanotubes (CNT) and biopolymers for microelectronic applications.