CHAPTER 4

SUMMARY AND CONCLUSION

The calcium containing monomers, calcium salt of mono(hydroxybutyl)phthalate $[\text{Ca(HBP)}_2]$ and calcium salt of mono(hydroxybutyl)hexolate $[\text{Ca(HBH)}_2]$ were synthesized by the reaction of 1,4-butane diol and calcium acetate with phthalic anhydride and hexolic anhydride respectively. Bisureas (TBHEU, HBHEU, TBHMPU and HBHMPU) were synthesized by the reaction of aminoalcohols (ethanolamine or 2-amino-2-methyl-propan-1-ol) with diisocyanate (HMDI or TDI).

Calcium containing PUs and PUUs having ionic links in the main chain were synthesized by the reaction of diisocyanate (HMDI or TDI) with $\text{Ca(HBP)}_2$ or $\text{Ca(HBH)}_2$ and 1:1 mixture of $\text{Ca(HBP)}_2$ or $\text{Ca(HBH)}_2$ and any of the bisureas (TBHEU, HBHEU, TBHMPU or HBHMPU). Blank PUUs without calcium content were synthesized by the polyaddition condensation reaction of diisocyanate (HMDI or TDI) with bisurea (TBHEU, HBHEU, TBHMPU or HBHMPU). A series of calcium containing PUE$_i$s having different composition were synthesized by taking the mole ratio of $\text{Ca(HBP)}_2$:PEG$_{200}$ or PEG$_{400}$:diisocyanate (HMDI or TDI) as 3:1:4, 2:2:4 and 1:3:4. Blank PUE$_i$s were synthesized by the reaction of PEG$_{200}$ or PEG$_{400}$ with diisocyanate (HMDI or TDI). A series of calcium containing PUEs having different composition were synthesized by taking the mole ratio of $\text{Ca(HBP)}_2$:HTPBG$_{1000}$:diisocyanate (HMDI or TDI) as 3:1:4, 2:2:4 and 1:3:4. Blank PUE$_i$s were synthesized by the reaction of HTPBG$_{1000}$ with diisocyanate (HMDI or TDI). A series of calcium containing PUE$_i$Es having different composition were synthesized by taking the mole ratio of $\text{Ca(HBP)}_2$:HTPDGP$_{350}$:diisocyanate (HMDI or TDI) as 3:1:4, 2:2:4 and 1:3:4.
Blank PUE,Es were synthesized by the reaction of HTPDGP\textsubscript{356} with diisocyanate (HMDI or TDI). The calcium containing polymers (PUs, PUUs, PUE\textsubscript{s}, PUE\textsubscript{s} and PUE,Es) and blank polymers were characterized by IR, \textsuperscript{1}H-NMR, \textsuperscript{13}C-NMR and Solid state \textsuperscript{13}C-CP-MAS NMR for structural confirmation. Molecular weights of blank polymers were determined by GPC.

Calcium containing polymers are insoluble in most of the organic solvents and soluble in highly polar solvents which infers the presence of ionic linkages. The inherent viscosity of calcium containing polymers are found to be low when compared with that of blank polymers which reveals that static linkages between COO\textsuperscript{-} and Ca\textsuperscript{2+} in the polymer chain dissociate into small fragments of low molecular weight. The HMDI based polymers show slightly higher viscosity than TDI based polymers. Calcium containing PUUs derived from HMDI based bisurea, HMDI and Ca(HBP\textsubscript{2}) or Ca(HBH\textsubscript{2}) show slightly higher viscosity than those derived from TDI based bisureas, TDI and the ionic diols. The viscosity of the calcium containing PUE\textsubscript{s}, PUE\textsubscript{s} and PUE,Es increases with increase in the soft segment content as well as its length and decreases with increase in calcium content. Polymers with higher amount of calcium content and lower amount of soft segment content dissociate into small molecular weight fragments in DMSO and hence exhibit lower viscosity. With increase in the soft segment content and its unit length and decrease in calcium content in the polymer, the viscosity increases due to presence of lower number of ionic linkages. The PUE\textsubscript{s} based on PEG\textsubscript{400} has higher viscosity than those based on PEG\textsubscript{300}. The PUE\textsubscript{s} based on HTPBG\textsubscript{1800} has higher viscosity than PUE\textsubscript{1}Es based on HTPDGP\textsubscript{356}.

Experimentally determined percentage values of carbon, hydrogen and calcium content for the calcium containing PUs are well with in the calculated values. The experimentally determined percentage values of carbon and hydrogen are little higher for calcium containing PUUs than the
calculated value assuming that 1:1 ratio of Ca(HBP)$_2$ or Ca(HBH)$_2$ and any of the bisureas were used up in the synthesis of PUUs. But the calcium content in PUUs are found to be less than the calculated value showing that the reactivity of bisureas are higher than that of the ionic diols.

The IDT of the calcium containing polymers are lower than that of blank polymers. Also, the IDT of HMDI based polymers are lower than TDI based polymers as the latter case has rigid aromatic ring. In general the residual weight at 750°C corresponds to CaO formed for the polymers based on Ca(HBP)$_2$. The residual weight at 800°C corresponds to the calcium compounds and char formed for the polymers based on Ca(HBH)$_2$. The IDT of the calcium containing polymers (PUEs, PUEs or PUEtEs) increases with decrease in calcium content. The blank polymers show slightly higher IDT than calcium containing polymers, but the decomposition rate is higher than calcium containing polymers. The PUEs based on PEG$_{400}$ has higher IDT than PUEs based on PEG$_{200}$. The decomposition take place at the urethane linkages and the number of urethane linkages are more in the PUEs based on PEG$_{200}$ than PUEs based on PEG$_{400}$. The PUEs based on PEG$_{400}$ exhibit lower IDT than those derived from PEG$_{400}$ this may be due to the presence of higher percentage of calcium ions in the former which catalyses the first stage decomposition. In general, calcium containing PUEs show slightly higher IDT than calcium containing PUEtEs.

The $T_g$ values of the TDI based polymers are slightly higher than HMDI based polymers. The HMDI based polymer is expected to show much lower $T_g$ than TDI based polymers. But, due to partial crystallinity of HMDI based polymers, the $T_g$ values are not much lower than expected. The polymers derived from Ca(HBH)$_2$ show lower $T_g$ value than those derived from Ca(HBP)$_2$. This can be due to the presence of few bulky groups (hexolic acid moiety) in the polymer chain decreases the intermolecular attraction between the chains. The $T_g$ value of calcium containing PUUs are higher than calcium containing PUs. This may be due to greater hydrogen bonding
interactions due to the urea, urethane and ester linkages in the polymeric chain. The PUUs based on HBHMPU and TBHMPU show higher $T_g$ value than PUUs based on HBHEU and TBHEU this can be explained due to presence of methyl groups attached to main backbone which leads to chain entanglement.

The $T_g$ value of polymers (PUE$s$, PUE$s$ or PUE$t$Es) increases with increase with calcium content and decreases with increase in soft segment content and length. A single $T_g$ value is observed for the PUE$s$ based on PEG$_{200}$ and PUE$t$Es based on HTPDGP$_{356}$ for various composition of Ca(HBP)$_2$:PEG$_{200}$ or HTPDGP$_{356}$:diisocyanate, indicating phase mixing of the soft segment with the ionic species and the hard segment. Two $T_g$ values for the PUE$s$ based on PEG$_{400}$ and PUE$s$ based on HTPBG$_{1000}$ for various composition of Ca(HBP)$_2$:PEG$_{400}$ or HTPBG$_{1000}$:diisocyanate (HMDI or TDI) show the presence of heterogenous phase. The first $T_{g1}$ value can be considered for soft segment and second $T_{g2}$ value can be considered for the phase mixing due to soft segment, ionic species and hard segment.

The LOI values of the calcium containing PUs and PUUs based on Ca(HBH)$_2$ indicate that they exhibit flame retardant characteristics. The flame retardant property of the hexolic acid based calcium containing polymers is due to the flame being cooled by the hexachloropentadiene which was formed by a retro Diels-Alder reaction and by various other rearranged products formed during decomposition. The HMDI based flame retardant polymers have lower LOI value than TDI based polymers, because of the easy combustible nature of aliphatic chain than the aromatic ring in the polymeric chain. The PUUs in general exhibit lower LOI value than the PUs, due to presence of less amount of hexolic acid moiety in the copolymers. The PUUs formed from Ca(HBH)$_2$, TDI based bisurea and TDI show higher LOI value than those carried out from Ca(HBH)$_2$, HMDI based bisurea and HMDI. PUUs derived from HBHMPU and TBHMPU show lower LOI value than those derived from HBHEU and TBHEU due to the
higher combustible nature of HBHMPU or TBHMPU than HBHEU or TBHEU.

X-ray diffraction pattern of the polymers show that the HMDI based polymers are partially crystalline and TDI based polymers are amorphous in nature. The HMDI based polymers owe their tendency to crystallize to the presence of -(CH₂)₆ units in the backbone of the polymers.

The dynamic mechanical analysis of the calcium containing PUEₐₐ, PUEs and PUEₐEs based on HMDI show that with increase in the ionic content of polymer, modulus (g' and g'') increases at any given temperature. The magnitude of decrease in the modulus (g' and g'') with increase in temperature is found to be less for polymers with higher ionic content. The polymers without calcium content show lower modulus at any given temperature. The higher value of the storage modulus (g') for higher amount of ionic content are probably related to the formation of physical crosslinks in the copolymer system and as the ionic concentration in the polymer increases the ionic cluster forming capacity also increases which in turn increases the modulus. A rubbery plateau is noted for all the polymers above the first Tₜ. The variable composition of ionic and soft segment content in the polymer system has influence on the plateau height in the rubbery state. Soft rubbery state with lower plateau value of g' is observed for the system with higher amount of soft segment or without ionic species. Hard rubbery state with higher plateau value of g' is observed for the system with higher ionic content.

Calcium & chlorine containing polymers which were used as fillers in the epoxy resin adhesives show better LSS value. Adhesive formulations with fillers having higher ionic linkages show higher LSS value, due to static ionic linkages between Ca'' and COO' which increases the adhesive properties to a greater extent.