CHAPTER 5
CONCLUSION

- High thermal stability is a very desirable property in high performance polymers. Modifying the epoxy backbone in the DGEBA with diisocyanates results in the formation of a linear polymer – the oxazolidone.
- These novel modified epoxies have been synthesised by reacting diisocyanates with diepoxies.
- They are known as oxazolidone modified epoxies and are a result of polyaddition reaction between diisocyanates and diepoxies.
- Poly oxazolidones are characterized by higher thermal stability as compared with epoxy resin (DGEBA). A series of experiments were conducted to introduce the heterocyclic oxazolidone ring across the DGEBA backbone using diisocyanates (Tolylene diisocyanate -TDI and Methylene diisocyanate -MDI)
- Thermal stability was determined by thermogravimetric analysis (TGA) and it was found that thermal stability as compared to epoxy resin (DGEBA) was enhanced in oxazolidones by 33-35%.
- TGA studies showed that pure DGEBA degrades at $280^0\text{C}$, but the synthesized oxazolidone degrades between $360 - 380^0\text{C}$.
- A detailed study of degradation kinetics was conducted and the order of reaction was observed to be unity in all cases. using Coats and Redfern equation.
- In the study of kinetics, it was found that the energy of activation ($E_a$) of pure DGEBA was 34 K J mol$^{-1}$, while that of oxazolidones was between 48 KJ mol$^{-1}$ and 72 K J mol$^{-1}$. 
Various catalysts were used for oxazolidone synthesis – Tetrabutyl Ammonium Bromide, Ethyl Methyl Imidazole (EMI), Benzyl DiMethyl Amine (BDMA), DiButyl Tin Dilaurate (DBTL) and Tri Phenyl Phosphene (TPP).

- Of these, Tetrabutyl Ammonium Bromide showed better results as compared with BDMA and EMI.
- Both DBTL and TPP did not prove to be effective catalyst as no oxazolidone was formed when these were used in oxazolidone synthesis.
- Both N methyl Pyrolidone (NMP) and Dimethyl Formamide (DMF) were effective solvents for oxazolidone synthesis.
- On the basis of experimental findings, it was observed that tolylene diisocyanate gave better thermal stability, as compared to MDI and also TDI had better film producing qualities.
- Reactions were conducted both in bulk and in solution.
- The oxazolidones formed were always accompanied by the presence of urethane and isocyanurate which resulted in crosslinking, when reactions were conducted in bulk phase. This was confirmed by FTIR analysis which showed jumbled peak in the region 1710 cms\(^{-1}\) to 1754 cms\(^{-1}\).
- This indicates the presence of urethane, trimer and oxazolidone in the reaction mixture.
- The presence of trimer causes the formation of a crosslinked structure which immobilises the reaction mixture.
- Tetrabutyl Ammonium bromide proved to be the most successful catalyst used because higher thermal stability, absence of side products and highest yield was observed when it was used. Though EMI is an effective catalyst
but it gives considerable degree of homopolymerization, resulting in crosslinking of the linear polymer.

- Oxazolidone is a linear polymer and better results were observed when DMF, or NMP were used as solvent, and though higher temperatures can be maintained using NMP, there was not much difference in the properties of the oxazolidones formed when either of the solvent were used.

- On crosslinking with (BTDA), oxazolidones made using TDI showed better compatibility and the curing was faster and at lower temperature as compared with MDI, irrespective of the catalyst system used.

- The yield of oxazolidone was studied as a function of temperature. It was observed that yield was maximum between temperatures 160 – 180°C and it was lower at lower temperatures and no oxazolidone was found at temperatures below 90°C.

- Very specific conditions of temperature and an inert gas atmosphere had to be maintained during experiments. Presence of moisture leads to the formation of urethane or trimer instead of oxazolidone. Hence all glassware and chemicals used must be moisture free.

- Stoichiometric molar ratios were also studied for monomers for oxazolidone synthesis. The molar ratios studied were 1:1, 1.5:1, and 2:1 for epoxy and isocyanate.

- Best results were obtained when the ratio of the monomers used was 1:1:5 of Isocyanate and DGEBA respectively. This molar ratio gave higher thermal stability and minimum weight loss during degradation.

- Maximum yield was observed when the reaction temperature was maintained between 160°C-180°C. This was attributed to the fact that the
• Catalyst used functions only at this temperature while urethane and trimer is formed at lower temperatures.

• The oxazolidones synthesized both in bulk and in solution were characterized using FTIR, epoxy estimation and isocyanate estimation.

• FTIR characterization of oxazolidones synthesized in solution showed a sharp clear peak for oxazolidone carbonyl at 1754 cm\(^{-1}\) and absence of peaks for urethane and trimer. This FTIR peak was observed using various catalyst, isocyanate and solvent systems used indicating the presence of oxazolidone in all cases.

• Isocyanate estimation, showed no presence of isocyanurate in the reaction mixture and this result was consistent with FTIR study which also showed the absence of a peak for isocyanurate at 2270 cm\(^{-1}\).

• Epoxy estimation showed a residual epoxy in the solution, which was also, observed in the FTIR spectra, as a small peak, very much reduced at 914 cm\(^{-1}\).

• The oxazolidone synthesized was insoluble in acetone methanol, etc. and soluble in DMF.

• The reaction of DGEBA with diisocyanates was found to be complete in two hours and FTIR analysis showed that no change in spectra occurred if the reaction was continued further. Blends were prepared where the oxazolidone and the dianhydride were varied. The linear oxazolidones were crosslinked using aromatic dianhydrides. Both BTDA and PMDA were used and oxazolidone curing studies were done using DSC techniques.

• Various amounts of oxazolidone (mole %) were used to determine the optimum amount required for curing reaction.
The mole ratio of BTDA was also varied with respect to oxazolidone.

DSC analysis showed one single sharp peak during cure and this stands for a compatible system where only one product was formed and no other side products were formed.

BTDA proved to be a better hardener, because of both the ease in formation of blends and the highest heat of formation per mole was observed when the ratio of the oxazolidone to hardener was 0.4 mole % and the oxazolidone content was between 10% - 15%.

Excess anhydride in the blend resulted in the splitting off of the hardener around its melting point and lower ratios of hardener gave lower heat of formation. This value was between 227 – 133 J/g per mole.

This may be attributed to the fact oxazolidones had to he dispersed in epoxy before the hardener was added.

Various amounts of oxazolidone were added to the hardener and it was found that 10-15 % of the oxazolidone in the blend was sufficient to give highest crosslinked density. Heat of reaction was found to decrease when oxazolidone in the blend was increased beyond 15%.

A tertiary amine (BDMA) was used as a catalyst for preparing the blend because aromatic amines do not react directly and have to be converted to a monoester before reaction.

The amount of catalyst (BDMA) must be kept between (1-5phr) as an excess of it will result in crosslinking before the reaction and too little will not let the hardener react with the oxazolidone.
• The results obtained when blends were prepared using PMDA showed that there was not much change in the observed values of heat of reaction, onset temperature, end point and Tend, as compared to curing with BTDA.

• Thermogravimetric Analysis studies showed that cured resins using up to 0.3 % of the oxazolidone in the blend was sufficient to give maximum increase in thermal stability. It was also observed that 0.4mole ratio of the hardener was enough to increase thermal stability. This was because Heat of reaction in the blends increases as oxazolidone content increases.

• These crosslinked oxazolidones were insoluble in water and most organic solvents and showed poor solubility even on boiling with Methyl Ethyl Ketone and Dimethyl Formamide. Hence oxazolidones have been successfully proved to be better modified epoxies with characteristic higher thermal stability that can be of use in coatings foams, composites and laminates.

• These linear oxazolidones can be successfully cured using dianhydrides so that they can be of use in high performance thermosets.