

## Synthesis and characterization of oxazolidones with improved thermal stability

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### ABSTRACT

To increase thermal stability for high performance applications of epoxy resin system – Diglycidal Ether of bisphenol-A (DGEBA), the epoxy backbone is modified to incorporate aromatic and heterocyclic rings i.e. the oxazolidone ring. FTIR studies were conducted during the synthesis at various intervals. Appearance of peak at  $1754\text{ cm}^{-1}$  confirms the presence of oxazolidone ring and absence of peak at  $915\text{ cm}^{-1}$  and  $1730\text{ cm}^{-1}$  in the reaction mixture confirms complete consumption of epoxy groups and absence of trimeric isocyanate in the modified resin. Study of char yield during TGA studies indicates that as compared to 5% char yield in unmodified resin, the char yield in oxazolidone modified resin is 25–28%, thus confirming the higher thermal stability of modified epoxy resin. The present work indicates that thermal stability of modified epoxy increased in the range of 27.9% - 35.5%. The activation energy  $E$  and order of reaction ( $n$ ) was calculated by Coats and Redfern equation. Overall value of  $E$  lies in the range  $41.8 - 118.3\text{ KJ mol}^{-1}$ .

**Keywords:** Oxazolidone modified epoxy resin, Diglycidal ether of bisphenol-A, Diisocyanates, higher thermal stability, kinetics of thermal degradation.

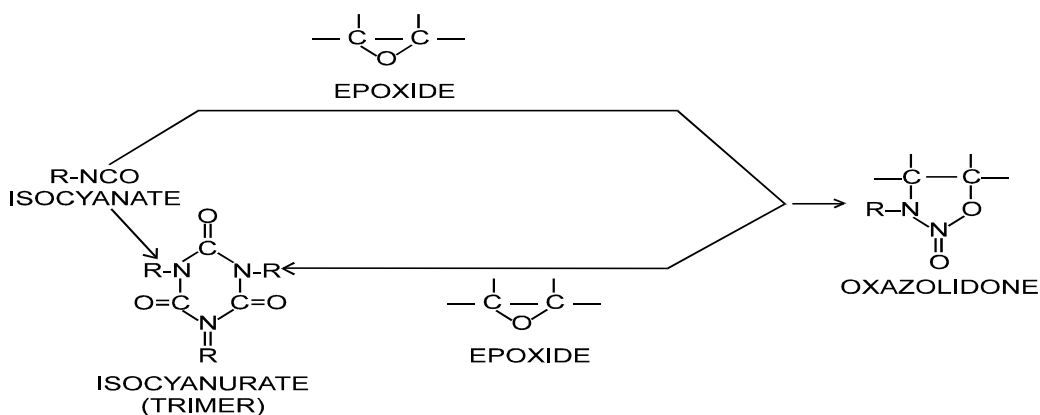
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### INTRODUCTION

Polyoxazolidones are polymers with improved thermal stability [1-3]. Varshney Etal[4,5,6] reported polymers of high thermal stability initiated by ylides or charge transfer complex Today, polymers with higher thermal properties are very much in demand for use in coatings and varnishes. The fast curing of high performance resins are thermosetting systems, are based on aromatic polyisocyanates and liquid diglycidal ether type epoxies. After mixing, the resulting resins are low viscosity fluids, at room temperature. Oxazolidone formation is a fairly complex [7,8] reaction due to the high competitive triisocyanurate formation. Reaction parameters such as type of reactants, reaction temperature, solvent and the selection of the appropriate catalyst has an important role in the synthesis of oxazolidones. The highly selective catalysts give a high yield of the desirable oxazolidone product at lower temperatures. The competitive reaction to the oxazolidone formation is the triisocyanurate which is a crossed linked polymer instead of the desired linear one.

This paper describes the preparation of a number of poly 2 oxazolidones, using different molar ratios of the isocyanate. Also, some polymers previously reported [8-14] were synthesized for comparison and characterization. The identification of the reaction products as poly 2 oxazolidones is based on FTIR studies. Thermal studies and char yields were also observed for changes in thermal stability.

The general scheme for the synthesis of oxazolidones is as follows:

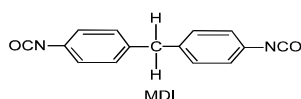


### EXPERIMENTAL

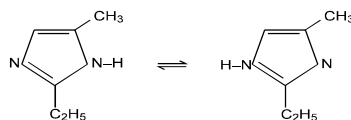
1) Synthesis of linear oxazolidones using Diglycidal ether of bisphenol A (DGEBA) and tolylene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI) so that heterocyclic oxazolidone ring is incorporated in the epoxy backbone.

2) Characterization of the linear polymer using FTIR, TGA studies to determine the thermal stability of the modified polymer.

NCO equivalent of isocyanates – 33.6 (as determined by excess DBA method)



Ethyl methyl imidazoles (EMI)



By varying either the catalyst concentration or the isocyanate to epoxy ratio, oxazolidones with improved thermal properties can be synthesized as follows:

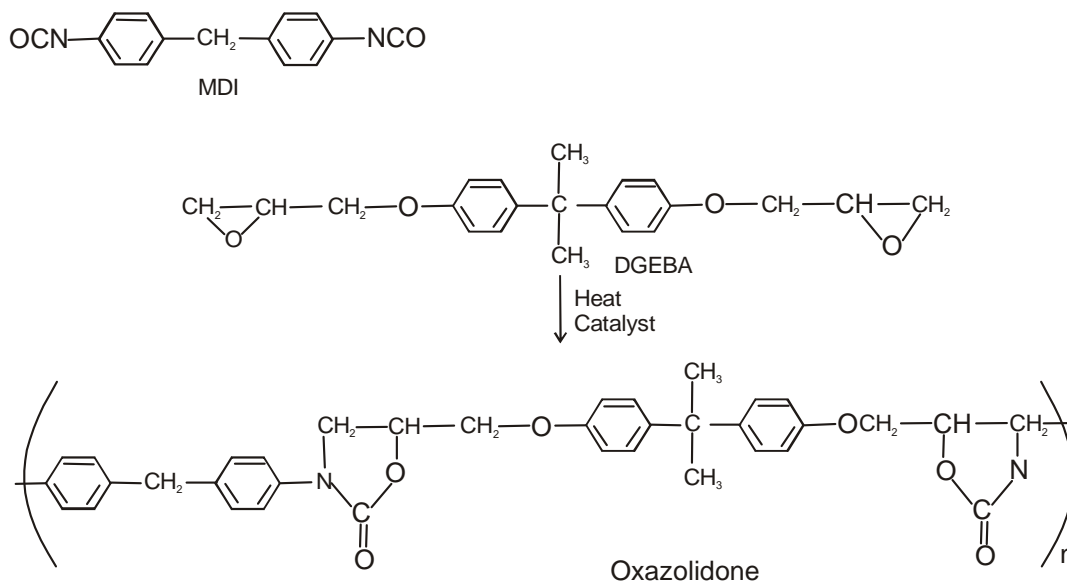


Table-I

S.No.	Resin	Isocyanate	Catalyst	Solvent
1.	DGEBA	TDI	Tetrabutyl Ammonium Bromide	DMF
2.	DGEBA	TDI	Ethyl Methyl Imidazole	NMP
3.	DGEBA	MDI	EMI	NMP
4.	DGEBA	TDI	BDMA	DMF
5.	DGEBA	MDI	BDMA	NMP

### Synthesis of oxazolidone

A three necked flask was fitted with a condenser, magnetic stirrer and pressure equalizing dropping funnel was weighed and 5.73 gms (0.002 moles) of DGEBA was added. Then 0.037 gms of the catalyst (0.1% by weight of the combined monomers) was added into the flask. 10 ml of the solvent was added, with the help of a syringe and stirred while being flushed with dry nitrogen gas for one hour. The temperature was gradually raised with continuous stirring to 180<sup>o</sup> -185<sup>o</sup>C, using an oil bath. 2.50 gms (0.002 moles) of the isocyanate dissolved in 10ml of the solvent was added drop wise over a period of one hour. The mixture was maintained at 180<sup>o</sup>C for 4 hours and then cooled gradually.

The viscous mixture from the flask was poured into 400ml of dry and distilled methanol and vigorously stirred for 10 minutes. A colloidal suspension appeared and a few drops of saturated NH<sub>4</sub>Cl in methanol were added while stirring.

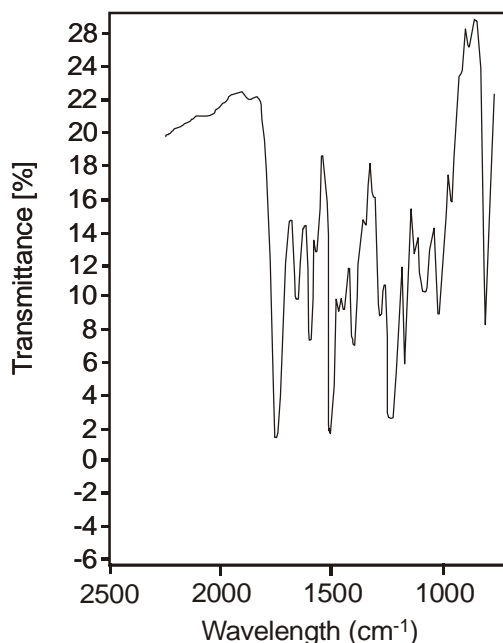
The precipitate observed was filtered and dried. It was dried in a vacuum oven at 40<sup>o</sup>C for six hours. This polymer was soluble in DMF, THF, and DMSO.

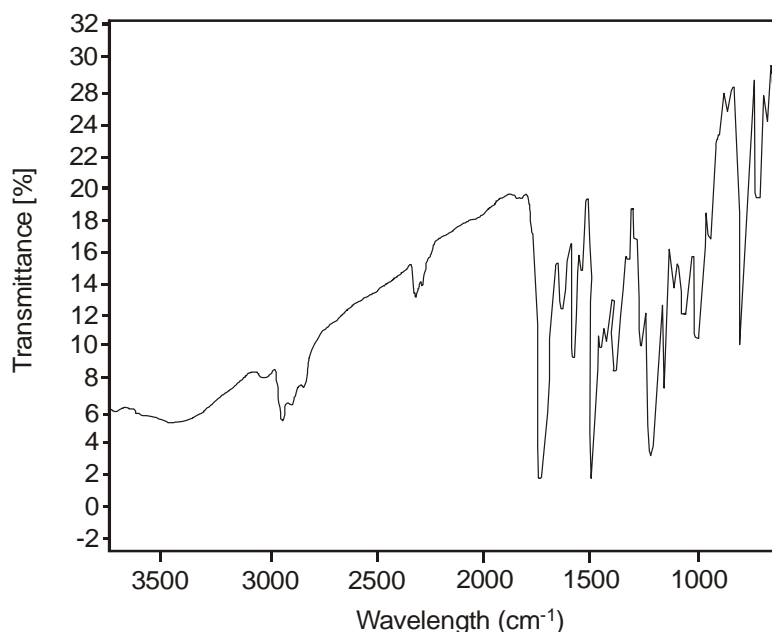
This reaction was repeated using different isocyanate, catalysts and solvents.

### FTIR Characterization

According to literature the FTIR peaks are assigned as follows:

- 1) 2270 cm<sup>-1</sup> - isocyanate peak
- 2) 1754 cm<sup>-1</sup> - oxazolidone peak
- 3) 1710 cm<sup>-1</sup> - isocyanurate peak
- 4) 910 cm<sup>-1</sup> - epoxy peak





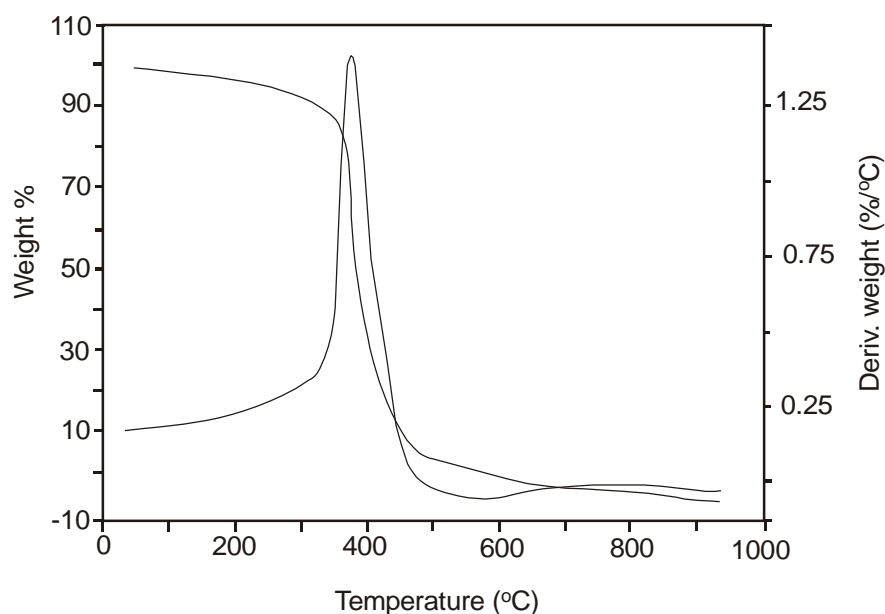
### TGA Studies

The increase in thermal stability (Table III) when compared to neat epoxy system is due to incorporation of oxazolidone in the epoxy resin backbone.

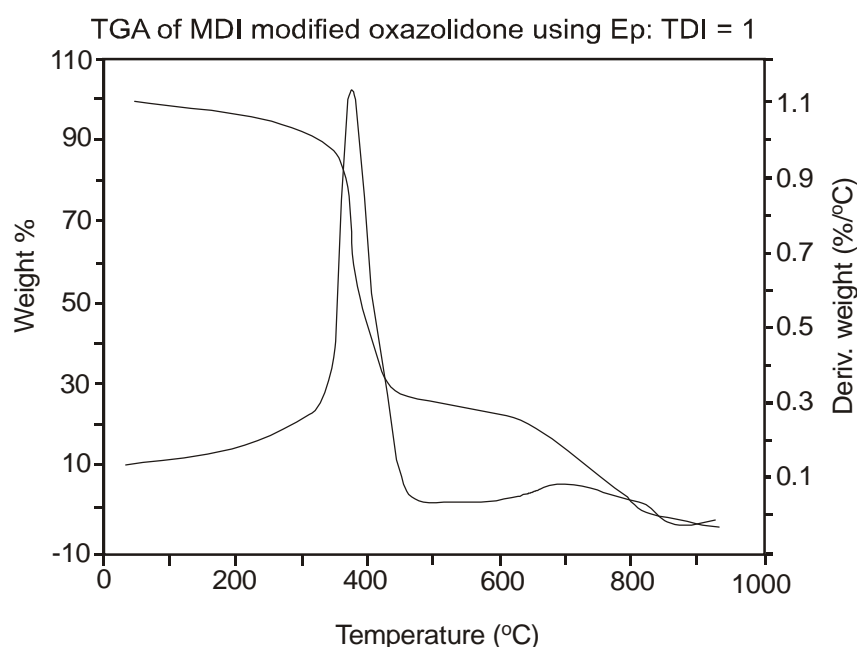
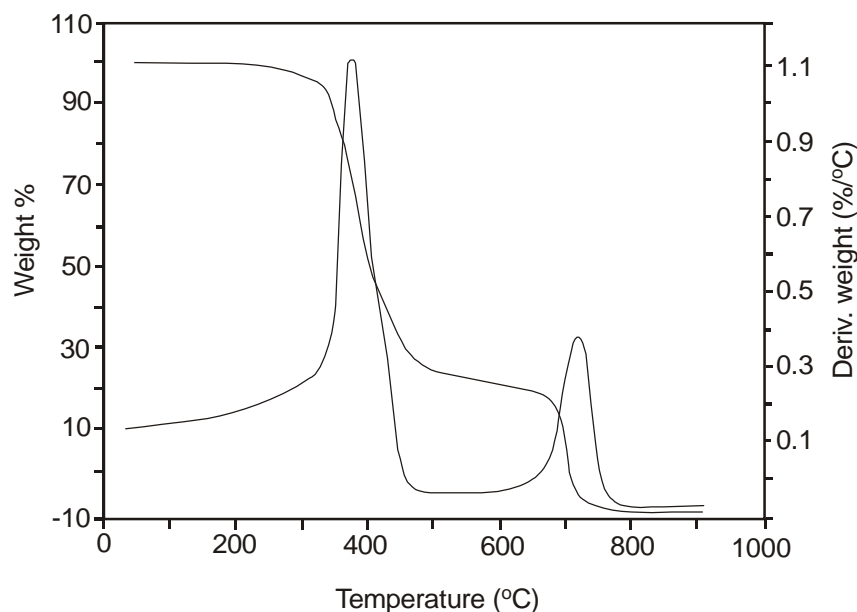
These results indicate that with increase in molar ratio of 1/E, the onset of temperature, midpoint and  $t_{end}$  increases. This increase in the thermal stability for 1:1 molar ratio, when compared with epoxy is 2.7%, 33% for 1:1.5 ratio and 35% for 1:2 molar ratio.

TABLE-II TGA RESULTS OF OXAZOLIDONE MODIFIED EPOXY RESIN

S. No.	Epoxy composition	Onset Temp.	Midpoint (°C)	$T_{end}$ (°C)	DTG <sub>max</sub> (°C)	Char yield % at 900°C
1.	Neat Epoxy	274.09	287.94	381.96	392.18	0.3049
2.	Epoxy+TDI (2:1)	371.62	392.29	708.77	380.09	2.33
3.	Epoxy+TDI (1.5:1)	216.00	379.00	756.97	372.96	4.16
4.	Epoxy+TDI (1:1)	183.00	367.95	657.43	385.00	4.70
5.	Epoxy+TDI (1.5:1) cat=BDMA	226.00	386.07	676.22	385.46	1.210
6.	Epoxy+TDI (1.5:1) Cat=EMI	379.00	396.00	704.00	402.73	2.463
7.	Epoxy+MDI (1:1) cat=EMI	346.73	402.00		386.63	7.170
8.	Epoxy+MDI (1.5:1) cat=BDMA		386.12	732.82		1.81



TGA of oxazolidone modified epoxy resin using Ep: TDI = 2.00



TGA of oxazolidone modified epoxy resin using Ep : TDI = 0.5

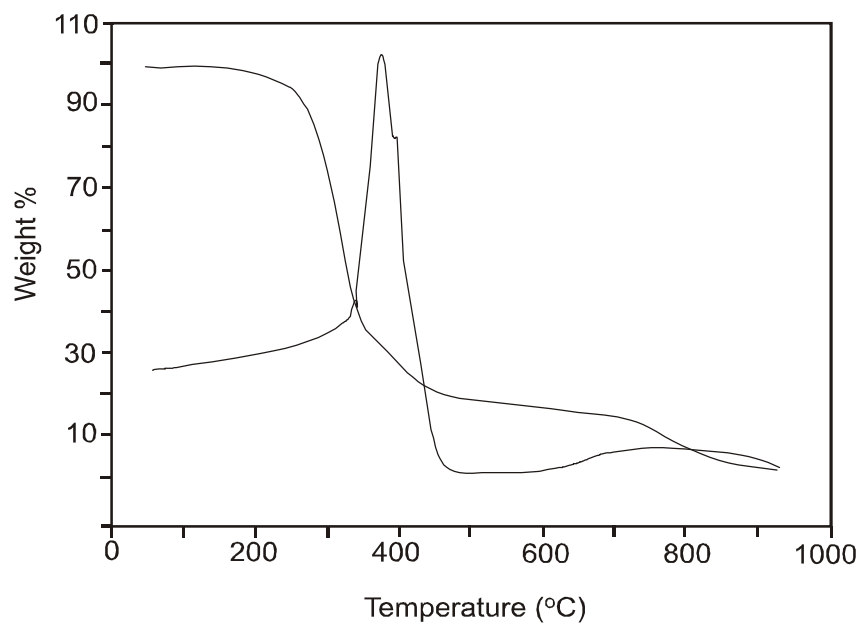
## RESULTS AND DISCUSSION

### Effect of temperature on yield:

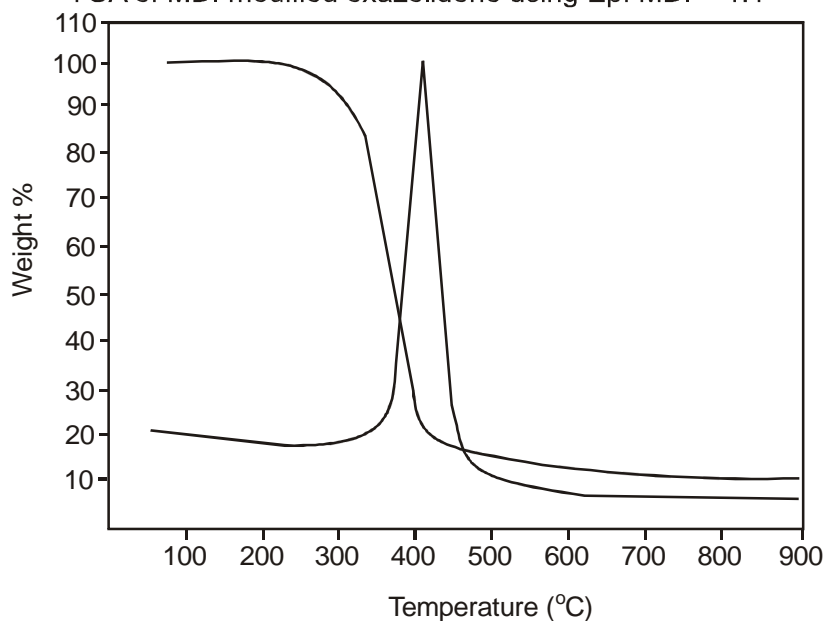
The effect of temperature was studied from ambient to 180°C. The epoxy ring is a highly strained very reactive group. In the presence of initiators, the epoxy ring opens at temperatures between 160°C to 180°C. Due to the reaction with the extremely reactive isocyanate group, poly addition reaction occurs. It is the ring strain that is considered the principal driving force in the polymerization of the cyclic monomers. At lower temperatures, the catalyst will not react and the isocyanate will produce a trimer and lead to the cross linking of the system.

Table-III Effect of temperature of yield

Composition (1:1) Ratio	Catalyst (0.5% by weight of monomer)	Reaction temperature	Yield (%)
DGEBA+TDI	Tetrabutyl ammonium bromide	30°C	Polymer trimerises
DGEBA+TDI	Tetrabutyl ammonium bromide	90°C	Polymer trimerises
DGEBA+TDI	Tetrabutyl ammonium bromide	120°C	31.4%
DGEBA+TDI	Tetrabutyl ammonium bromide	150°C	59.4%
DGEBA+TDI	Tetrabutyl ammonium bromide	180°C	65.5%



TGA of MDI modified oxazolidone using Ep: MDI = 1:1



TGA of MDI modified oxazolidone using Ep : MDI = 1:1.5

The stoichiometric ratio strongly influences the structure of the synthesized polymer, in the presence of a catalyst.

Table-IV Increase in thermal stability of modified epoxy resin

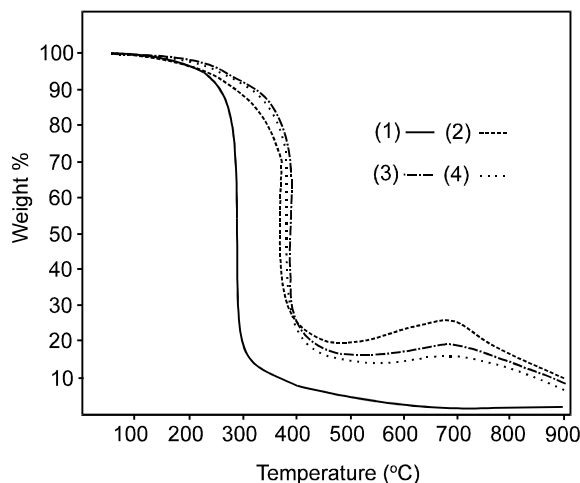
S.No.	Composition I/E ratio	Onset temperature	% Increase in thermal stability
1.	1:1	76.49	27.90
2.	1:1.5	92.03	33.58
3.	1:2	97.53	35.53

Table-V : Weight loss (%)

Composition	20% (°C)	25% (°C)	50% (°C)	75% (°C)	90% (°C)	Char Yield
Neat resin	290.30	292.06	297.00	310.00	360.00	0.30%
1:1.0	350.58	370.06	410.88	615.00	680.00	1.47%
1:1.5	380.00	380.00	395.04	595.09	790.00	4.1%
1:2.0	360.01	375.02	395.20	450.30	725.90	2.32%

Thermogravimetric analysis (TGA) studies were observed on Hi. Res. TGA 2950- Thermogravimetric analyzer-TA instruments. The dynamic TGA curves were obtained at heating rate of 10<sup>0</sup>C/min.

The TGA studies include the study of char yield and weight retention by the resin after pyrolysis. From the calculation of percentage of weight retention from TGA thermogram, it was found that the neat resin degraded 85% at 290.30<sup>0</sup>C., which is the standard degradation temperature of DGEBA, according to references [3]. However, the oxazolidone modified resin degraded 85% at 350.80<sup>0</sup>C for 1:1 molar ratio, 380.0<sup>0</sup>C for 1:1.5 molar ratio, and 360.01<sup>0</sup>C for 1:2 molar ratio. In all of these studies, the epoxy resin was reacted with TDI, with tetra butyl ammonium bromide as a catalyst and DMF was used as a solvent.



#### Degradation of pure epoxy. (Di glycidal ether of Bisphenol A)

Degradation starts at 274.09<sup>0</sup>C and the DTG peak is at 288.05<sup>0</sup>C.

When I/E molar ratio is 2:1, the onset of degradation is 371.62<sup>0</sup>C, with DTG maxima at 392.18<sup>0</sup>C. Hence, the thermal stability of oxazolidone as compared to pure epoxy has been enhanced. The DTG peak observed is very sharp, indicating the purity of the oxazolidone. The char residue is 2.33% as compared to 0.30% of neat resin.

Table-VI Reaction of DGEBA using MDI and EMI (catalyst)

S.No.	Composition I/E ratio	Onset Temp (°C)	Midpoint Temp (°C)	End Temp (°C)	Char Yield at 600°C
1.	Neat Resin	274.09	288.05	295.88	5%
2.	1:1	346.73	386.10	431.62	25%
3.	1:1.5	379.31	402.62	415.62	25%
4.	1:2.0	371.62	392.29	416.08	28%

**Studies on char yield:** Char formation occurs at the end of pyrolysis. Char yield depends on the chemical structure of the material. By modifying the DGEBA molecule using aromatic isocyanates like MDI and TDI, the aromatic character of the epoxy is increased and hence there should be an increase in char yield. This is proved in table IV where the char yield in the unmodified epoxy is 5% and in the modified epoxy it is between 25% to 28%.

Table-VII Characterization I.R. peaks of oxazolidone modified epoxy resin

Exp. No.	Epoxide (Moles)	Isocyanate (Moles)	Catalyst 0.5% (gm)	Solvent	Time	Temp. °C	Characteristics IR peak
1.	DGEBA -----1	TDI ---- 1	TBABr	DMF	2 hrs	160	1754.21 cm <sup>-1</sup>
2.	DGEBA -----2	TDI --- 1	TBABr	DMF	2 hrs	160	1754.21 cm <sup>-1</sup>
3.	DGEBA -----1.5	TDI -----1	TBABr	DMF	2 hrs	160	1754.21 cm <sup>-1</sup>
4.	DGEBA -----1.5	TDI ---1	BDMA	DMF	2 hrs	160	1754.22 cm <sup>-1</sup>
5.	DGEBA -----1.5	TDI ---1	EMI	NMP	2 hrs	160	1754.21 cm <sup>-1</sup>
6.	DGEBA -----1.5	MDI ---1	BDMA	NMP	2 hrs	180	1754.31 cm <sup>-1</sup>
7.	DGEBA -----1.5	MDI -----1	EMI	NMP	2 hrs	160	1754.5 cm <sup>-1</sup>

## CONCLUSION

High performance thermosetting resins with improved Thermal Stability are very useful in highly demanding environments to provide special properties. The stoichiometric ratio of the curing agent to epoxy resin in the blend becomes a very important factor in deciding the final material performance of the polymer.

This work is undertaken to make the synthesized polymer storage stable, and possess high melting point and high  $T_g$  (glass transition temperature). Its having high thermal resistance can be made use of in laminates and windings and high temperature resistant epoxy coatings and adhesives.

This is in keeping with the need today for a novel polymer because in this modern age of plastics, polymers having high thermal resistance find a very important and significant place.

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