

# **SYNTHESIS AND CHARACTERIZATION OF EPOXY-ZnO NANOCOMPOSITES**



A Dissertation submitted to the Department of Chemistry,  
Quaid-i-Azam University, Islamabad, in partial fulfillment of  
the

requirements for the degree of

**Master of Philosophy**

in

**Organic Chemistry**

by

**Tehmina Naz**

**Department of Chemistry**

**Faculty of Natural Sciences**

**Quaid-i-Azam University**

**Islamabad 2012**

## CERTIFICATE

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This is to certify that this dissertation entitled “*Synthesis and characterization of epoxy-ZnO nanocomposites*” submitted by *Miss Tehmina Naz* is accepted in its present form by the *Department of Chemistry, Quaid-i-Azam University, Islamabad*, as satisfying the dissertation requirement for the degree of *Master of Philosophy in Organic Chemistry*.

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He is Allah, whom there is none worthy of worship except He, the All-Knower of the unseen and the seen (open). He is the Most Beneficent, the Most Merciful. He is Allah, whom there is none worthy of worship except He, the King, the Holy, the One Free from all imperfections, the Giver of security, the Watcher over His creatures, the All-Mighty, the Compeller, the Supreme. Exalted is He above all that they associate [in worship] with Him. He is Allah, the Creator, the Inventor of all things, the Bestower of forms. To Him belong the Best Names. All that is in the heavens and the earth glorify Him. And He is the All- Mighty, the All-Wise.

(Al-Hashr 59:22-24)

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Prophet Muhammad (s) as reported by Abu Hurayrah, transmitted by  
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## **DEDICATION**

*I dedicate this work to my*

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*They shadowed me mean they were in*

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## ACKNOWLEDGEMENTS

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*First and foremost all praises and glory be to almighty Allah, the only creator of whole universe, the Most benevolent & most merciful, who created us as muslim and blessed us with knowledge to differentiate between right and wrong. Countless salutations upon the Holy Prophet Hazrat Muhammad (P.B.U.H), the source of knowledge and blessings for entire mankind, who exhorted his Ummah to seek for knowledge from cradle to grave.*

*I owe my deep gratitude and feel great pleasure and privilege to pay my profound respects to my inspirational and encouraging Supervisor **Dr. Mrs. Humaira Masood Siddiqi**, Associate Prof. Department of chemistry, QAU Islamabad, for her personal interest, thought provoking guidance, valuable suggestions, patience, motivation, enthusiasm, immense knowledge and discussions. Her guidance helped me in all the time of research and writing of this thesis. I feel lucky to be her student.*

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## ABSTRACT

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The polymer based nanocomposites have been the exceptionally growing field of research for developing the materials in the last few decades and have been mainly focusing the thermal stability, stiffness and tensile properties of composites materials. In the present work, as-synthesized and calcined ZnO NPs were used as particulate reinforcement in an epoxy matrix. ZnO NPs were synthesized by coprecipitation method. Size of these NPs was tuned from 9nm-70nm by varying time and temperature of reaction. These particles were characterized by IR, UV, XRD, TGA, SEM and PL. As-synthesized ZnO NPs have promising optical, luminescent and photocatalytic activity.

From the range of different sized particles obtained, two sizes were selected for incorporation into composites films. Organic-inorganic nanocomposites were synthesized from Diglycidyl ether of bisphenol A (DER332) epoxy resin and 2,2'-dimethyl-4,4'-diaminodicyclohexylmethane. Four series of nanocomposites were synthesized by varying the percentage of ZnO NPs. These composite systems were characterized by Fourier transformed infrared microscopy (FT-IR), Differential Scanning Calorimetry (DSC), X-Ray Diffraction Analysis (XRD), Ultra Violet Spectroscopy (UV) & Scanning Electron Microscopy (SEM). ZnO NPs were well dispersed in composites films forms three-dimensional network of epoxy-amine nanocomposites network as characterized by SEM. Differential scanning calorimetry revealed an increase of glass transition temperature  $T_g$  as wt% of particles increases. Even a small amount of ZnO NPs was beneficial to increase the  $T_g$  of composite from 91°C to 100°C. These nanocomposites have high UV shielding properties.

## TABLE OF CONTENTS

Sr. No No.	CONTENTS	Page
	<b>Dedication</b>	
	<b>Acknowledgement</b>	
	<b>Abstract</b>	
	<b>CHAPTER 1: INTRODUCTION .....</b>	<b>1-32</b>
1.1	WHAT ARE COMPOSITES.....	1
1.1.1	CONSTITUENTS OF COMPOSITES.....	1
1.1.2	CHARACTERISTICS OF COMPOSITES.....	3
1.1.3	POLYMER MATRIX MATERIAL.....	4
1.2	EPOXY RESINS .....	5
1.2.1	CHARACTERISTICS OF EPOXY RESINS .....	6
1.2.2	TYPES OF EPOXY RESINS .....	7
1.2.2.1	GLYCIDYL EPOXY RESIN.....	8
1.2.2.1.1	Diglycidyl ether of bisphenol-A (DGEBA).....	8
1.2.2.1.2	Bisphenol F epoxy resins.....	9
1.2.2.1.3	Novolac epoxy resins.....	9
1.2.2.1.4	Polyglycol epoxy resins.....	10
1.2.2.1.5	Halogenated epoxy resins.....	10
1.2.2.2	NON-GLYCIDYL EPOXY RESIN.....	11
1.2.2.2.1	Cyclic aliphatic epoxy resins.....	11
1.2.2.2.2	Acyclic Aliphatic Epoxy resins.....	11
1.2.3	APPLICATIONS OF EPOXY RESINS.....	12
1.2.4	CROSS-LINKING.....	12
1.2.5	CROSS-LINKING DENSITY.....	13
1.2.6	CURING OF EPOXY RESINS .....	13
1.3	CURING AGENTS (HARDENERS).....	15
1.4	FILLERS AND REINFORCEMENTS .....	18
1.5	NANOTECHNOLOGY.....	19
1.5.1	NANOCOMPOSITES .....	20
1.6	ZINC OXIDE.....	21
1.6.1	CRYSTAL STRUCTURE.....	22
1.6.2	PROPERTIES OF ZnO NANOPARTICLES.....	23
1.6.3	APPLICATIONS OF ZINC OXIDE NANOPARTICLES.....	24
1.6.4	SYNTHESIS OF ZNO NPS BY CO-PRECIPI-TATION METHOD.....	25

1.6.5 CAPPING AGENT/ SURFACTANT .....	26
1.7 LITERATURE REVIEW .....	26
1.8 PLAN OF WORK.....	30
<b>CHAPTER 2: EXPERIMENT.....</b>	<b>33-41</b>
2.1 CHEMICALS USED .....	33
2.1.1 SOLVENT USED.....	34
2.2 CHARACTERIZATION TECHNIQUES .....	34
2.2.1 FOURIER TRANSFORM INFRA-RED SPECTROSCOPY (FTIR): .....	34
2.2.2 X-RAY DIFFRACTION ANALYSIS (XRD) .....	34
2.2.3 ULTRA-VIOLET SPECTROSCOPY (UV-vis) .....	34
2.2.5 DIFFERENTIAL SCANNING CALORIMETRY (DSC).....	34
2.2.6 THERMOGRAVIMETRIC ANALYSIS (TGA) .....	34
2.2.7 SCANNING ELECTRON MICROSCOPY (SEM) .....	34
2.3 EXPERIMENTAL.....	35
2.3.1 SYNTHESIS OF ZnO NANOPARTICLES .....	35
2.3.1.1 PROCEDURE.....	36
2.3.2 SYNTHESIS OF COMPOSITES .....	37
2.3.2.1 SYNTHESIS OF NEAT EPOXY-AMINE NETWORK (TN-NEAT) ....	37
2.3.2.2 SYNTHESIS OF EPOXY-ZINC OXIDE NANOCOMPOSITES.....	38
2.3.2.2.1 Procedure .....	38
2.3.2.2.2 Series 1 (TTN 01) .....	39
2.3.2.2.3 Series 02: (TTN02) .....	40
2.3.2.2.4 Series 03: (TTN03) .....	40
2.3.2.2.5 Series 04: (TTN 04) .....	41
<b>CHAPTER 3: RESULTS AND DISCUSSION .....</b>	<b>42-60</b>
3.1 PARTICLES ANALYSIS .....	42
3.1.1 PHYSICAL APPEARANCE .....	42
3.1.2 FT-IR SPECTROSCOPY .....	42
3.1.3 X-RAY DIFFRACTION ANALYSIS .....	45
3.1.4 ULTRA VIOLET SPECTROSCOPY .....	49
3.1.5 PHOTOLUMINESCENCE SPECTROSCOPY.....	51
3.1.6 THERMOGRAVIMETRIC ANALYSIS .....	52
3.1.7 SCANNING ELECTRON MICROSCOPY .....	53
3.2 CHARACTERIZATION OF ZNO NANOCOMPOSITE SYSTEMS .....	54
3.2.1 FT-IR SPECTROSCOPY .....	55
3.2.2 X-RAY DIFFRACTION ANALYSIS OF NANOCOMPOSITES.....	57
3.2.3 SCANNING ELECTRON MICROSCOPY OF NANOCOMPOSITES.....	57
3.2.4 UV ANALYSIS OF NANOCOMPOSITES.....	59

3.2.5 THERMAL ANALYSIS .....	60
3.2.5.1 DIFFERENTIAL SCANNING CALORIMETRY OF EPOXY-AMINE NEAT.....	61
<b>Conclusion</b> .....	
63	
<b>Future</b>	
<b>Plan</b> .....	64
<b>References</b> .....	
65	

## LIST OF FIGURES

---

Figure 1.1: Classification of composite materials.....	2
Figure 1.2: Ethylene oxide.....	5
Figure 1.3: Structures of glycidyl and non-glycidyl epoxy resin.....	8
Figure 1.4: Classification of epoxy resin.....	8
Figure 1.5: Diglycidyl ether of bisphenol A.....	9
Figure 1.6: Bisphenol F epoxy resin.....	9
Figure 1.7: Structure of novolac epoxy resin.....	9
Figure 1.8: Structure of polyglycol epoxy resin.....	10
Figure 1.9: Halogenated epoxy resin.....	10
Figure 1.10: Cyclic aliphatic epoxy resins.....	11
Figure 1.11: Termolecular transition state of the epoxy-amine addition in the presence of hydroxyl containing groups.....	14
Figure 1.12: Mechanism of epoxy-amine curing.....	15
Figure 1.13: Aliphatic and aromatic amine curing agents.....	16
Figure 1.14: Important commercial anhydrides.....	17
Figure 1.15: Tetrahedral structure of ZnO structure.....	22
Figure 1.16: Hexagonal wurtzite structure of ZnO.....	22
Figure 1.17: Rock salt and zinc blende structure of ZnO phases.....	23
Figure 1.18: Structure of surface functionalized ZnO nanoparticles.....	30
Figure 1.19: A general scheme showing probable reaction of Epoxy- amine ZnO network....	32
Figure 2.1: Diglycidyl ether of bisphenol A DGEBA (DER-332) n=0.03.....	33
Figure 2.2: 2, 2'-Dimethyl-4, 4'-diaminodicyclohexylmethane.....	33
Figure 2.4: Schematic representation showing synthesis of uncalcined ZnO nanoparticles ....	36
Figure 2.5: Schematic representation of epoxy-amine neat network.....	38
Figure 2.6: A general equation showing synthesis of TN-neat.....	38
Figure 2.7: Schematic representation of epoxy-amine-ZnO nanocomposites.....	39
Figure 3.1: IR spectra of calcined and un-calcined ZnO NPs.....	43
Figure 3.2: XRD of ZnO nanoparticles.....	45
Figure 3.3: XRD peak correlation of ZnO with the reference.....	46
Figure 3.4: Size of nanoparticles Vs growth time a) 60°C b) 94°C.....	47
Figure 3.5: Size of nanoparticles Vs reaction temperature.....	49
Figure 3.6: UV-vis spectrum of ZnO nanoparticles.....	50
Figure 3.7: Comparative UV spectra of ZnO nanoparticles.....	51
Figure 3.8: Photoluminescence spectrum of ZnO nanoparticles.....	52
Figure 3.9: TGA of ZnO nanoparticles.....	53
Figure 3.10: SEM image of surface functionalized ZnO nanoparticles.....	53
Figure 3.11: FTIR spectrum of epoxy-amine network.....	55
Figure 3.12: Combine FTIR spectra of epoxy amine network and zinc oxide epoxy amine nanocomposites.....	56

Figure 3.13: XRD plots of ZnO, ZnO epoxy-amine nanocomposites and epoxy-amine neat network.....	57
Figure 3.14: SEM image of epoxy-amine ZnO nanocomposites.....	58
Figure 3.15: UV-vis spectra of ZnO nanocomposites.....	60
Figure 3.16: T <sub>g</sub> of TTN 03-2.....	62

## LIST OF TABLES

---

Table	2.1:	Variation in time and temperature for synthesis of ZnO.....	37
Table	2.2:	Composition Wt% of TTN 01.....	40
Table	2.3:	Composition Wt% of TTN 02.....	40
Table	2.4:	Composition Wt% of TTN 03.....	41
Table	2.5:	Composition Wt% of TTN 04.....	41
Table	3.1:	IR frequencies of surface functionalized ZnO NPs.....	44
Table	3.2:	Relationship between growth time and nanoparticles size at 60°C.....	48
Table	3.3:	Relationship between growth time and nanoparticles size at 94°C.....	48
Table	3.4:	Relationship between temperature and nanoparticles size.....	49
Table	3.5:	IR frequencies of epoxy-amine neat.....	56
Table	3.6:	T <sub>g</sub> values for the epoxy nanocomposites at different nano-ZnO concentrations for TTN 03.....	61

## LIST OF STANDARD ABBREVIATIONS

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<b>DGEBA</b>	Diglycidyl ether of bisphenol-A
<b>NPs</b>	Nanoparticles
<b>MACM</b>	2,2'-dimethyl-4,4'-diaminodicyclohexylmethane
<b>DETA</b>	Diethylenetriamine
<b>TETA</b>	Triethylenetetramine
<b>DDS</b>	4,4'-diaminodiphenylsulphine
<b>CNTs</b>	Carbon nanotubes
<b>eV</b>	Electron volts
<b>LED</b>	Light emitting diodes
<b>POM</b>	Polyoxymethylene
<b>UV</b>	ultra violet spectroscopy
<b>FTIR</b>	Fourier transform infra-red spectroscopy
<b>XRD</b>	X-ray diffraction analysis
<b>PL</b>	Photoluminescent spectroscopy
<b>TGA</b>	Thermogravimetric analysis
<b>SEM</b>	Scanning electron microscopy
<b>DSC</b>	Differential scanning calorimetry
<b>nm</b>	Nanometer
<b>hr</b>	hour/s
<b>min</b>	minute/s





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## TABLE OF CONTENTS

Sr. No	CONTENTS	Page No.
	<u>Dedication</u>	
	Acknowledgement	
	Abstract	
	<b>CHAPTER 1: INTRODUCTION</b> .....	<b>1-32</b>
<u>1.1</u>	<u>WHAT ARE COMPOSITES</u> .....	1
<u>1.1.1</u>	<u>CONSTITUENTS OF COMPOSITES</u> .....	1
<u>1.1.2</u>	<u>CHARACTERISTICS OF COMPOSITES</u> .....	3
<u>1.1.3</u>	<u>POLYMER MATRIX MATERIAL</u> .....	4
<u>1.2</u>	<u>EPOXY RESINS</u> .....	5
<u>1.2.1</u>	<u>CHARACTERISTICS OF EPOXY RESINS</u> .....	6
<u>1.2.2</u>	<u>TYPES OF EPOXY RESINS</u> .....	7
<u>1.2.2.1</u>	<u>GLYCIDYL EPOXY RESIN</u> .....	8
<u>1.2.2.1.1</u>	<u>Diglycidyl ether of bisphenol-A (DGEBA)</u> .....	8
<u>1.2.2.1.2</u>	<u>Bisphenol F epoxy resins</u> .....	9
<u>1.2.2.1.3</u>	<u>Novolac epoxy resins</u> .....	9
<u>1.2.2.1.4</u>	<u>Polyglycol epoxy resins</u> .....	10
<u>1.2.2.1.5</u>	<u>Halogenated epoxy resins</u> .....	10
<u>1.2.2.2</u>	<u>NON-GLYCIDYL EPOXY RESIN</u> .....	11
<u>1.2.2.2.1</u>	<u>Cyclic aliphatic epoxy resins</u> .....	11
<u>1.2.2.2.2</u>	<u>Acyclic Aliphatic Epoxy resins</u> .....	11
<u>1.2.3</u>	<u>APPLICATIONS OF EPOXY RESINS</u> .....	12
<u>1.2.4</u>	<u>CROSS-LINKING</u> .....	12
<u>1.2.5</u>	<u>CROSS-LINKING DENSITY</u> .....	13
<u>1.2.6</u>	<u>CURING OF EPOXY RESINS</u> .....	13
<u>1.3</u>	<u>CURING AGENTS (HARDENERS)</u> .....	15
<u>1.4</u>	<u>FILLERS AND REINFORCEMENTS</u> .....	18
<u>1.5</u>	<u>NANOTECHNOLOGY</u> .....	19
<u>1.5.1</u>	<u>NANOCOMPOSITES</u> .....	20

<u>1.6 ZINC OXIDE</u> .....	21
<u>1.6.1 CRYSTAL STRUCTURE</u> .....	22
<u>1.6.2 PROPERTIES OF ZnO NANOPARTICLES</u> .....	23
<u>1.6.3 APPLICATIONS OF ZINC OXIDE NANOPARTICLES</u> .....	24
<u>1.6.4 SYNTHESIS OF ZNO NPS BY CO-PRECIPIATION METHOD</u> .....	25
<u>1.6.5 CAPPING AGENT/ SURFACTANT</u> .....	26
<u>1.7 LITERATURE REVIEW</u> .....	26
<u>1.8 PLAN OF WORK</u> .....	30
<b><u>CHAPTER 2: EXPERIMENT</u></b> .....	<b>33-41</b>
<u>2.1 CHEMICALS USED</u> .....	33
<u>2.1.1 SOLVENT USED</u> .....	34
<u>2.2 CHARACTERIZATION TECHNIQUES</u> .....	34
<u>2.2.1 FOURIER TRANSFORM INFRA-RED SPECTROSCOPY (FTIR):</u> .....	34
<u>2.2.2 X-RAY DIFFRACTION ANALYSIS (XRD)</u> .....	34
<u>2.2.3 ULTRA-VIOLET SPECTROSCOPY (UV-vis)</u> .....	34
<u>2.2.5 DIFFERENTIAL SCANNING CALORIMETRY (DSC)</u> .....	34
<u>2.2.6 THERMOGRAVIMETRIC ANALYSIS (TGA)</u> .....	34
<u>2.2.7 SCANNING ELECTRON MICROSCOPY (SEM)</u> .....	34
<u>2.3 EXPERIMENTAL</u> .....	35
<u>2.3.1 SYNTHESIS OF ZnO NANOPARTICLES</u> .....	35
<u>2.3.1.1 PROCEDURE</u> .....	36
<u>2.3.2 SYNTHESIS OF COMPOSITES</u> .....	37
<u>2.3.2.1 SYNTHESIS OF NEAT EPOXY-AMINE NETWORK (TN-NEAT)</u> .....	37
<u>2.3.2.2 SYNTHESIS OF EPOXY-ZINC OXIDE NANOCOMPOSITES</u> .....	38
<u>2.3.2.2.1 Procedure</u> .....	38
<u>2.3.2.2.2 Series 1 (TTN 01)</u> .....	39
<u>2.3.2.2.3 Series 02: (TTN02)</u> .....	40
<u>2.3.2.2.4 Series 03: (TTN03)</u> .....	40
<u>2.3.2.2.5 Series 04: (TTN 04)</u> .....	41
<b><u>CHAPTER 3: RESULTS AND DISCUSSION</u></b> .....	<b>42-60</b>
<u>3.1 PARTICLES ANALYSIS</u> .....	42
<u>3.1.1 PHYSICAL APPEARANCE</u> .....	42
<u>3.1.2 FT-IR SPECTROSCOPY</u> .....	42

<a href="#"><u>3.1.3 X-RAY DIFFRACTION ANALYSIS</u></a> .....	<a href="#"><u>45</u></a>
<a href="#"><u>3.1.4 ULTRA VIOLET SPECTROSCOPY</u></a> .....	<a href="#"><u>49</u></a>
<a href="#"><u>3.1.5 PHOTOLUMINESCENCE SPECTROSCOPY</u></a> .....	<a href="#"><u>51</u></a>
<a href="#"><u>3.1.6 THERMOGRAVIMETRIC ANALYSIS</u></a> .....	<a href="#"><u>52</u></a>
<a href="#"><u>3.1.7 SCANNING ELECTRON MICROSCOPY</u></a> .....	<a href="#"><u>53</u></a>
<a href="#"><u>3.2 CHARACTERIZATION OF ZNO NANOCOMPOSITE SYSTEMS</u></a> .....	<a href="#"><u>54</u></a>
<a href="#"><u>3.2.1 FT-IR SPECTROSCOPY</u></a> .....	<a href="#"><u>55</u></a>
<a href="#"><u>3.2.2 X-RAY DIFFRACTION ANALYSIS OF NANOCOMPOSITES</u></a> .....	<a href="#"><u>57</u></a>
<a href="#"><u>3.2.3 SCANNING ELECTRON MICROSCOPY OF NANOCOMPOSITES</u></a> .....	<a href="#"><u>57</u></a>
<a href="#"><u>3.2.4 UV ANALYSIS OF NANOCOMPOSITES</u></a> .....	<a href="#"><u>59</u></a>
<a href="#"><u>3.2.5 THERMAL ANALYSIS</u></a> .....	<a href="#"><u>60</u></a>
<a href="#"><u>3.2.5.1 DIFFERENTIAL SCANNING CALORIMETRY OF EPOXY-AMINE NEAT</u></a> .....	<a href="#"><u>61</u></a>
<b>Conclusion</b> .....	<b>6</b>
3	
<b>Future Plan</b> .....	<b>64</b>
<b>References</b> .....	<b>6</b>
5	

## LIST OF FIGURES

---

Figure 1.1: Classification of composite materials .....	2
Figure 1.2: Ethylene oxide.....	5
Figure 1.3: Structures of glycidyl and non-glycidyl epoxy resin.....	8
Figure 1.4: Classification of epoxy resin.....	8
Figure 1.5: Diglycidyl ether of bisphenol A .....	9
Figure 1.6: Bisphenol F epoxy resin .....	9
Figure 1.7: Structure of novolac epoxy resin .....	9
Figure 1.8: Structure of polyglycol epoxy resin .....	10
Figure 1.9: Halogenated epoxy resin .....	10
Figure 1.10: Cyclic aliphatic epoxy resins.....	11
Figure 1.11: Termolecular transition state of the epoxy-amine addition in the presence of hydroxyl containing groups.....	14
Figure 1.12: Mechanism of epoxy-amine curing .....	15
Figure 1.13: Aliphatic and aromatic amine curing agents .....	16
Figure 1.14: Important commercial anhydrides .....	17
Figure 1.15: Tetrahedral structure of ZnO structure .....	22
Figure 1.16: Hexagonal wurtzite structure of ZnO. ....	22
Figure 1.17: Rock salt and zinc blende structure of ZnO phases .....	23
Figure 1.18: Structure of surface functionalized ZnO nanoparticles .....	30
Figure 1.19: A general scheme showing probable reaction of Epoxy- amine ZnO network ....	32
Figure 2.1: Diglycidyl ether of bisphenol A DGEBA (DER-332) n= 0.03.....	33
Figure 2.2: 2, 2'-Dimethyl-4, 4'-diaminodicyclohexylmethane.....	33
Figure 2.4: Schematic representation showing synthesis of uncalcined ZnO nanoparticles....	36
Figure 2.5: Schematic representation of epoxy-amine neat network.....	38
Figure 2.6: A general equation showing synthesis of TN-neat .....	38
Figure 2.7: Schematic representation of epoxy-amine-ZnO nanocomposites .....	39
Figure 3.1: IR spectra of calcined and un-calcined ZnO NPs.....	43

Figure 3.2: XRD of ZnO nanoparticles .....	45
Figure 3.3: XRD peak correlation of ZnO with the reference.....	46
Figure 3.4: Size of nanoparticles Vs growth time a) 60°C b) 94°C .....	47
Figure 3.5: Size of nanoparticles Vs reaction temperature .....	49
Figure 3.6: UV-vis spectrum of ZnO nanoparticles .....	50
Figure 3.7: Comparative UV spectra of ZnO nanoparticles .....	51
Figure 3.8: Photoluminescence spectrum of ZnO nanoparticles.....	52
Figure 3.9: TGA of ZnO nanoparticles.....	53
Figure 3.10: SEM image of surface functionalized ZnO nanoparticles.....	53
Figure 3.11: FTIR spectrum of epoxy-amine network.....	55
Figure 3.12: Combine FTIR spectra of epoxy amine network and zinc oxide epoxy amine nanocomposites.....	56
Figure 3.13: XRD plots of ZnO, ZnO epoxy-amine nanocomposites and epoxy-amine neat network.....	57
Figure 3.14: SEM image of epoxy-amine ZnO nanocomposites .....	58
Figure 3.15: UV-vis spectra of ZnO nanocomposites.....	60
Figure 3.16: T <sub>g</sub> of TTN 03-2.....	62

## LIST OF TABLES

---

Table 2.1: Variation in time and temperature for synthesis of ZnO.....	37
Table 2.2: Composition Wt% of TTN 01.....	40
Table 2.3: Composition Wt% of TTN 02.....	40
Table 2.4: Composition Wt% of TTN 03.....	41
Table 2.5: Composition Wt% of TTN 04.....	41
Table 3.1: IR frequencies of surface functionalized ZnO NPs.....	44
Table 3.2: Relationship between growth time and nanoparticles size at 60°C.....	48
Table 3.3: Relationship between growth time and nanoparticles size at 94°C.....	48
Table 3.4: Relationship between temperature and nanoparticles size.....	49
Table 3.5: IR frequencies of epoxy-amine neat.....	56
Table 3.6: T <sub>g</sub> values for the epoxy nanocomposites at different nano-ZnO concentrations for TTN 03.....	61



## LIST OF STANDARD ABBREVIATIONS

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<b>DGEBA</b>	Diglycidyl ether of bisphenol-A
<b>NPs</b>	Nanoparticles
<b>MACM</b>	2,2'-dimethyl-4,4'-diaminodicyclohexylmethane
<b>DETA</b>	Diethylenetriamine
<b>TETA</b>	Triethylenetetramine
<b>DDS</b>	4,4'-diaminodiphenylsulphine
<b>CNTs</b>	Carbon nanotubes
<b>eV</b>	Electron volts
<b>LED</b>	Light emitting diodes
<b>POM</b>	Polyoxymethylene

<b>UV</b>	ultra violet spectroscopy
<b>FTIR</b>	Fourier transform infra-red spectroscopy
<b>XRD</b>	X-ray diffraction analysis
<b>PL</b>	Photoluminescent spectroscopy
<b>TGA</b>	Thermogravimetric analysis
<b>SEM</b>	Scanning electron microscopy
<b>DSC</b>	Differential scanning calorimetry
<b>nm</b>	Nanometer
<b>hr</b>	hour/s
<b>min</b>	minute/s

## INTRODUCTION

---

In the quest for improved performance, which may be specified by various criteria including more strength, lower cost and less weight, currently used materials frequently reach the limit of usefulness. Scientist and engineers are always striving to produce either improved traditional materials, with better properties or completely new material, composites and especially nanocomposites are the example of later category.

### 1.1 WHAT ARE COMPOSITES?

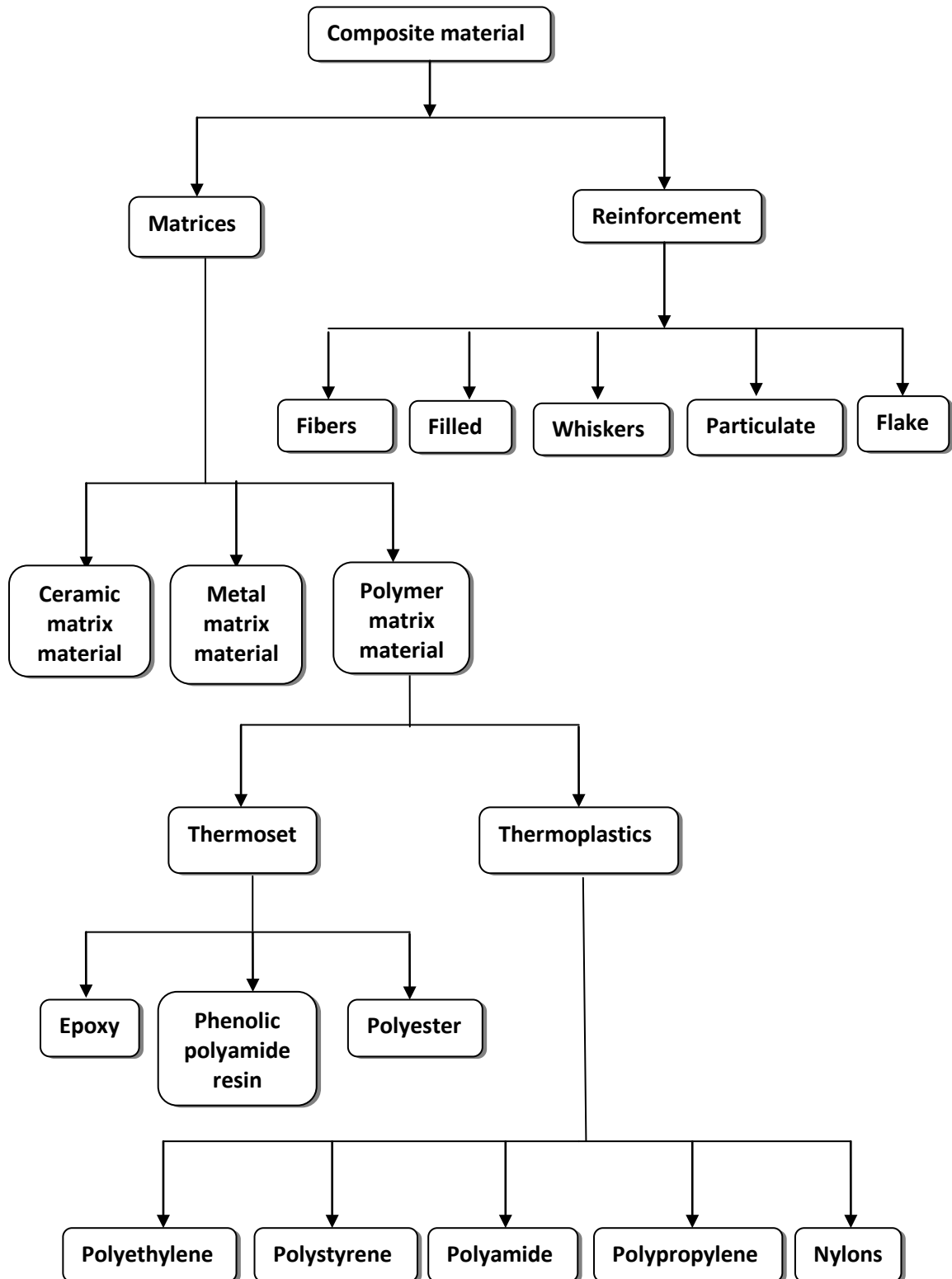
**Composite materials**, often shortened to **composites**, are engineered or naturally occurring materials made from two or more constituents with significantly different physical or chemical properties. Wood is a natural composite material consisting of cellulose fibers, which provide good strength and stiffness to the matrix of another polymer, the polysaccharide lignin. The earliest man-made composite materials were the bricks made up of straw and mud to enhance the structural integrity of their building. Bone, teeth and mollusc shells are examples of natural composites, in which hard ceramic reinforcing phases combines with natural organic polymer matrices.

#### 1.1.1 CONSTITUENTS OF COMPOSITES

Composites are made up of at least two materials referred to constituent materials. These materials have two categories: One is matrix which is binding material and the other is the reinforcement material <sup>[1]</sup>. Matrix is a bulk material and the reinforcement material or filler is added primarily to increase the mechanical strength and stiffness of matrix but sometimes it also modify its thermal conductivity and electrical resistivity <sup>[2]</sup>.

The combination of dissimilar materials can have very advantageous and unique properties if the materials have appropriate characteristics, and the resultant material is better in certain key properties than either of the materials alone <sup>[3]</sup>. Composites are considered as heterogeneous system. Their performance depends upon electrical and mechanical properties of their constituents, geometric characteristics, size and spatial distribution of the filler within matrix. Interaction between the two constituents can also improve dielectric properties of composites <sup>[4]</sup>.

Classification of composite material is given in the figure. 1.1



**Figure 1.1: Classification of composite materials**

### 1.1.2 CHARACTERISTICS OF COMPOSITES

Composite materials have found expanded use in aerospace, marine and automobile industries during the past few decades due to their good properties such as high specific strength and stiffness, lower density high fatigue endurance, high damping and low thermal coefficient <sup>[5]</sup>. Some of these unique characteristics are elaborated below:

**a) Strength:**

One of the most important characteristics of the composite material is its strength. Due to their hardness and rigidity they provide the required strength for all the structures that they are used for. High strength, low weight and excellent design flexibility allows them to be easily molded into structures that have such requirements <sup>[6]</sup>.

**b) Stiffness:**

Another important characteristic of composites is their stiffness to density ratio. The stiffness usually depends on the spatial configuration of the reinforcements which helps in various structural applications.

**c) Corrosion resistance:**

Composite products provide long term resistance to severe chemical and temperature environments. Composites are material of choice for outdoor exposure, chemical handling applications and severe environment service <sup>[7]</sup>.

**d) Design flexibility:**

Composites materials have an advantage over other materials because they can be molded into complex shapes at relatively low cost. This property gives designers the freedom to create any shape or configuration <sup>[5]</sup>.

**e) Durability:**

Composites materials have an exceedingly long life span. Coupled with low maintenance requirements, the long life of composites is a benefit in critical applications. From a half century of composites development, well designed composites structures have yet to wear out <sup>[8]</sup>.

**f) Environmental sustainability:**

The use of composite material has reduced the impacts on the environment as it has minimized the use of various toxic compounds and increased the consumption of environment friendly products <sup>[7]</sup>.

### 1.1.3 POLYMER MATRIX MATERIAL

Polymer matrix composites consist of a polymer matrix reinforced with glass fibers and to a lesser extent carbon, boron and polyaramide fibers [2]. For the processing of polymer matrix composites there is no need of very high pressure and high temperature. Equipments required for manufacturing of polymer matrix composites are also simpler. Due to these reasons polymer matrix composites developed rapidly and soon became popular for structural applications. However the mechanical properties of polymers are inadequate for many structural purposes and in particular their stiffness and strength are low as compared to metals and ceramics. These difficulties are overcome by reinforcing polymer matrix with other materials [9].

Properties of polymers are improved by addition of inorganic fillers. Material properties of the composites are determined by both the constituents and thus depend upon the content of the filler, its adhesion to polymer matrix, uniformity of dispersion, etc. From the last two decades the varieties of thermosets, thermoplastics, linear or cross-linked systems have been reinforced with inorganic fillers, either formed *in situ* or *ex situ* [10-12].

According to structure and behavior, polymer matrices can be classified into thermoplastics and thermosets.

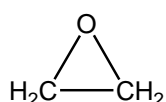
**Thermoplastics** consist of linear or branched chain molecules sharing a covalent bonding within each molecule and van der Waals forces between the molecules. They are semi-crystalline or amorphous in structure and the chain can move freely as the polymer is melted or softened. Important examples of thermoplastics are polyethylene, polyvinyl chloride, polystyrene, polypropylene, polyamide polyacetals and polyesters.

**Thermosetting polymers** have cross-linked structure with a network of covalent bond between molecules. They cannot be remelted or reshaped, when solidified by the cross-linking process. Thermosetting polymers are brittle material and are used in a variety of engineering applications because of high strength-to-weight ratio, excellent chemical resistance, weather ability and versatility of product design. Common examples include epoxy resins, phenolics, silicones, aminoplastics, and unsaturated polyester resins [13].

## 1.2 EPOXY RESINS

Epoxy resins are one of the most important classes of thermosetting polymers. These are characterized by high strength, high elastic modulus, strong bond ability and excellent chemical stability. These are widely used in the field of aerospace, automotive electronics and chemical engineering<sup>[14, 15]</sup>.

Epoxy refers to a chemical group consisting of an oxygen atom bonded to two carbon atoms. The simplest epoxy is a three membered ring, which is termed as  $\alpha$ -epoxy or 1,2-epoxy. Ethylene oxide is its simplest example as shown in figure 1.2. Epoxy resins are characterized by the presence of at least two epoxy groups or oxirane rings with in their molecular structure<sup>[16]</sup>.



**Figure 1.2: Ethylene oxide**

There is a controversy about the three membered epoxy rings. Americans used the term epoxy while the Europeans generally preferred the term epoxide, which is more correct. The term oxirane is the trivial name of the ethylene oxide. The epoxides may also be designated as oxides e.g., ethylene oxide (epoxyethane) or cyclohexene oxide(1,2-epoxy-, 1,2-oxidocyclohexane)<sup>[17]</sup>.

Epoxy resins are oligomeric compounds with oxirane groups, formed by the reaction of bisphenol A and epichlorohydrin comprising more than 90% of the world production<sup>[18]</sup>.

In commercial products the value of n ranges from 0 to about 25, although higher molecular weight thermoplastic resins have n value of 200 or more are available. As the value of n increases so does the number of hydroxyl groups. The epoxy resins with low values are normally cured by the reaction of epoxy group, whereas those resins with higher value of n are cured by reaction of the hydroxyl functionality<sup>[19]</sup>.

Epoxy resins with n value less than 1 are viscous liquids; they are used mainly in ambient-temperature cure coatings, electrical coatings, flooring, electrical laminates and fiber reinforced composites. The epoxy resins with higher value of n are particularly those above 3000 molecular weight. These are normally used in solution and find their greatest application in heat-cured coatings. In these resins the concentration of epoxy resins is low, so that they are cured with material that react with hydroxyl groups<sup>[20]</sup>.

### **1.2.1 CHARACTERISTICS OF EPOXY RESINS**

Epoxy resin is one of the most widely used thermoset polymer for a variety of applications including, aerospace, automotive, electronic, chemical engineering and in the synthesis of composites <sup>[15]</sup>. The rapid industrial growth of epoxy resins is conclusively due to their numerous marvelous properties.

#### **a) Low viscosity**

The epoxy resins and their curing agents form low viscosity and easy to process system. Viscosity is affected by the molecular weight, as the molecular weight increases epoxy resins become more viscous <sup>[21]</sup>.

#### **b) Low shrinkage**

The remarkable property of epoxy resins is its low shrinkage upon curing. This is because very little rearrangement takes place with no volatile by-product being evolved. The suppression or control of volume shrinkage during polymerization is of great important in the design of materials which requires precise dimensions or for the preparation of composites <sup>[22]</sup>.

#### **c) Easy Cure**

Epoxy resin can easily be cured with different curing agents at a wide range of temperature from 5°C to above 150°C <sup>[23]</sup>.

#### **d) High Adhesive Strength**

The adhesive strength of epoxy resin is attributed to its chemical composition. Presence of polar hydroxyl and ether groups prove that they have an excellent adhesive to various surfaces. Due to presence of oxygen atoms covalent bond formation between the polymer and substrate takes place which is the main reason of strong adhesion <sup>[24]</sup>.

#### **e) Good Chemical Resistance**

Most epoxy resins possess extremely high resistance to bases and a “good to excellent”, range of resistance to acids. Cured epoxies do not dissolve water or almost all solvents hence are not corroded.

#### **f) High Electrical insulation**



Epoxy resins have very high electrical insulation <sup>[25]</sup>. Therefore they have wide applications in electrical chip preparation.

#### **g) Excellent mechanical properties**

The strength of epoxy resin usually surpasses that of other type of resins. This is probably due to low shrinkage, which minimizes the stresses.

#### **h) Versatility**

Modification in basic molecular ring of epoxy resins can be done by substitution with different functional moieties. The basic properties of epoxy resins can be modified by either blending of resin or by selection of curing agents or by use of modifiers and fillers <sup>[26, 27]</sup>.

#### **i) Flame Retardants**

Epoxy resins are capable of being excellent flame retardants. Synergistic combination of nitrogen and phosphorus to hardeners leads to noteworthy improvement in flame resistance of cured DGEBA <sup>[28]</sup>.

#### **J) Corrosion resistance**

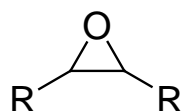
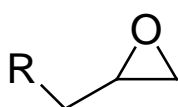
Epoxy coatings generally reduce the corrosion of a metallic object to an electrolyte in two ways. First, they act as a physical barrier layer to control the ingress of harmful species. Second, they can serve as a reservoir for corrosion inhibitors to aid the metal surface in resisting attack by aggressive species such as chloride anions <sup>[29]</sup>.

### **1.2.2 TYPES OF EPOXY RESINS**

Epoxy resins can be classified into two main categories:

1. Glycidyl epoxy resins
2. Non-glycidyl epoxy resins

In glycidyl type epoxy resins the epoxy group terminates at i.e., [-CH<sub>2</sub>-CHOCH<sub>2</sub>]. In non-glycidyl epoxy resins the epoxy group is present inside the molecule so that the molecule does not terminate at epoxy functionality. In such epoxies the oxirane group is present on both  $\alpha$  and  $\beta$  carbons.

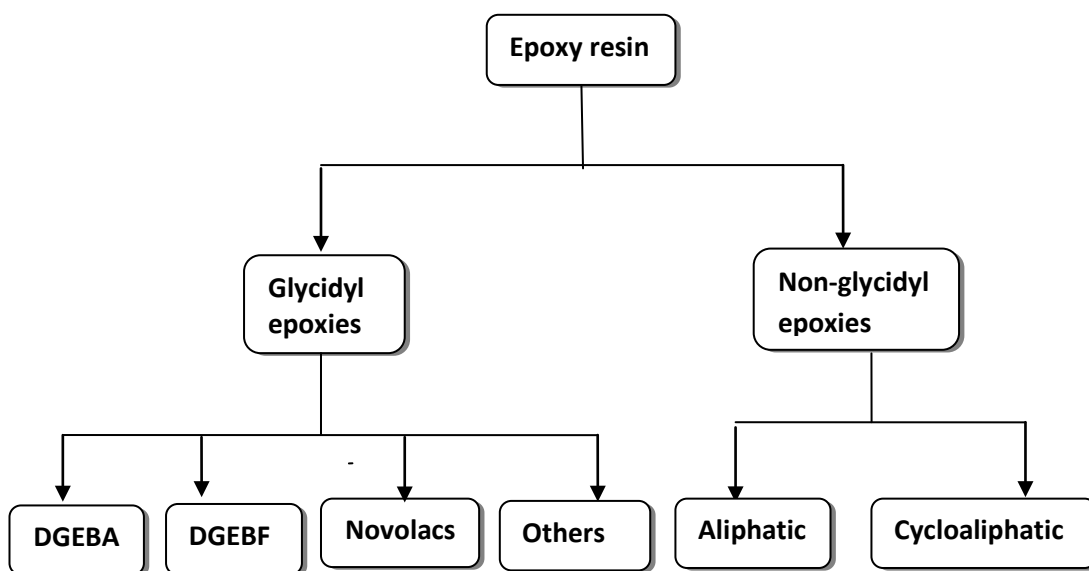


## Glycidyl epoxy

## Non- Glycidyl epoxy

**Figure 1.3: Structures of glycidyl and non-glycidyl epoxy resin**

Glycidyl epoxies are prepared via condensation reaction of dihydroxy compounds, dibasic acids or diamines with epichlorohydrin. Non-glycidyl epoxies are prepared by peroxidation of olefinic double bond <sup>[30, 31]</sup>. The classification of epoxy resin is described in figure 1.4.



**Figure 1.4: Classification of epoxy resin <sup>[32]</sup>**

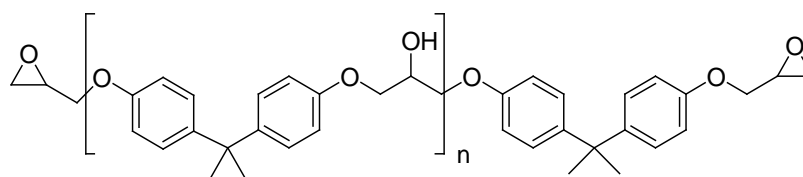
### 1.2.2.1 GLYCIDYL EPOXY RESIN

The presence of glycidyl epoxy group in epoxy resins imparts flexibility and serves to reduce the viscosity of the resin and thus helps to enhance its processability. Unfortunately, the heat resistance of cured epoxy resins also decreases by the presence of glycidyl epoxy groups, as the aliphatic linkage in glycidyl groups provides the source of early thermal and thermo-oxidative degradation of the cured epoxy system <sup>[33]</sup>.

#### 1.2.2.1.1 Diglycidyl ether of bisphenol-A (DGEBA)

Diglycidyl ether of bisphenol-A, as shown in figure 1.5 is typical commercially available epoxy synthesized by the reaction of bisphenol-A with epichlorohydrin, in the presence of a basic catalyst. It is the most important epoxy system due to its relative low viscosity, physical strength after curing and relatively low production cost. Bisphenols contain a wide variety of thermally stable rigid rings which have been used to synthesize high performance epoxy resins. Rigid rings are

particularly useful in preparation of resins with improved heat resistance and char formation <sup>[34]</sup>.

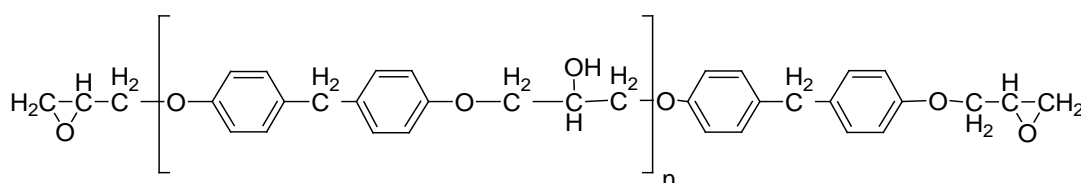


**Figure 1.5: Diglycidyl ether of bisphenol A**

The diglycidyl ether of bisphenol-A (DGEBA) has many attractive properties such as fluidity, low shrinkage during cure and ease of processing. The cured products have good physical strength, excellent moisture, solvent and chemical resistance <sup>[35]</sup>.

#### 1.2.2.1.2 Bisphenol F epoxy resins

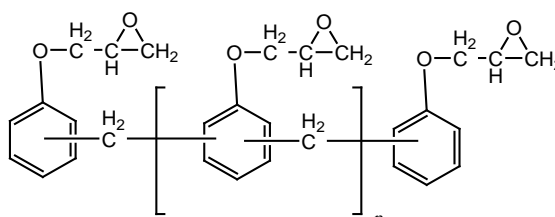
Diglycidyl ether of bisphenol-F is another type of glycidyl epoxy resin shown in figure 1.6. It is formed by the condensation reaction between epichlorohydrin and bisphenol-F in the presence of a base. This epoxy resin has a lower viscosity and more chemical resistance than most DGEBA resins. They do not have high molecular weight versions as in bisphenol-A epoxy resins.



**Fig 1.6: Bisphenol F epoxy resin**

#### 1.2.2.1.3 Novolac epoxy resins

Novolac epoxy resins are the glycidyl ethers of phenolic novolac resins shown in figure 1.7. Phenolic novolac resins are synthesized by the reaction of formaldehyde with excess of phenol in the presence of acidic catalyst. Novolac epoxy resins are synthesized by reacting epichlorohydrin with phenolic novolac resin in presence of sodium hydroxide as a catalyst.

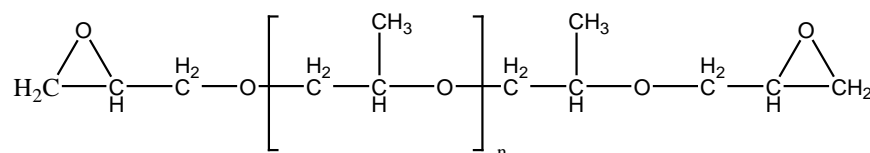


**Figure 1.7: Structure of novolac epoxy resin**

Novolac epoxy resins generally contain multiple epoxy groups. The number of epoxide group per molecule depends upon the number of phenolic –OH groups in the starting phenolic novolac resin, the extent to which they reacted and the degree of low molecular species being polymerized during synthesis. The multiple epoxide groups allow novolac resins to achieve high cross-link density resulting in excellent temperature, chemical and solvent resistance. These resins are widely used to formulate the molding compounds for microelectronics packaging because of their superior performance at elevated temperature, excellent mould-ability, and mechanical properties, superior electrical properties, and heat and humidity resistance [36].

#### 1.2.2.1.4 Polyglycol epoxy resins

Polyglycol epoxy resins, as shown in figure 1.8, are synthesized by the epichlorohydrin and polyglycol. Terminal hydroxyl group in the main chain leads to the epoxidation of polyglycol. Common example of polyglycol epoxy resin is polypropylene glycol.

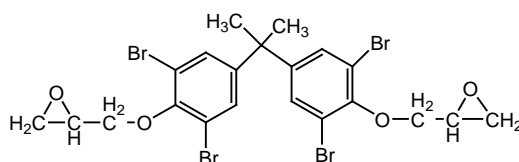


**Figure 1.8: Structure of polyglycol epoxy resin**

By incorporating, 10-30% of epoxy resins bisphenol A in this type of resins, better strength properties are obtained [37].

#### 1.2.2.1.5 Halogenated epoxy resins

Halogenated epoxy resins are synthesized by the reaction of halogenated hydroxyl compounds with epichlorohydrin. Commonly used halogenated compounds are tetrabromobisphenol A or tetrachlorobisphenol. The structure of halogenated epoxy resin is analogous with the epoxy resin based on bisphenol A except that halogen atoms are attached to its aromatic ring. Structure of halogenated epoxy resin is shown in figure 1.9



**Figure 1.9: Halogenated epoxy resin**

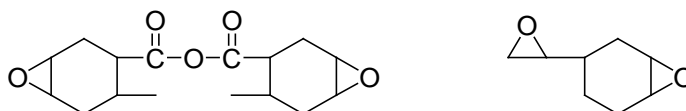
The presence of halogens makes these resins flame retardants. The flame retardency of these resins is due to the evolution of hydrogen halide upon decomposition at elevated temperature <sup>[38]</sup>.

### 1.2.2.2 NON-GLYCIDYL EPOXY RESIN

Non-Glycidyl ethers of epoxy resins have been produced by the epoxidation of olefinic linear or cyclic compounds. They are mainly used as reactive diluents of glycidyl ether epoxy. The epoxidation reaction involves the use of an olefinic compounds and a peracid e.g., peracetic acid or other oxidizing substances such as hydrogen peroxide, molecular oxygen or even air <sup>[39]</sup>. Non-Glycidyl epoxy resins include **cyclic** and **acyclic aliphatic** epoxies.

#### 1.2.2.2.1 Cyclic aliphatic epoxy resins

Cycloaliphatic epoxy resins possess an epoxy group that is internal to the ring rather than external. Some common examples are shown in figure 1.10.



(a) 3,4-Epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate

(b) 4-Vinylcyclohexane dioxide

**Figure 1.10: Cyclic aliphatic epoxy resins**

Cycloaliphatic epoxy resins possess high  $T_g$  as compared to other resins because the cross link formed by curing is linked directly to the cyclic backbone. These are more flexible than aromatic epoxy resins. Cycloaliphatic epoxy resins have recently been very important for the preparation of cured adhesives and coatings <sup>[40]</sup>.

#### 1.2.2.2.2 Acyclic Aliphatic Epoxy resins

Many aliphatic compounds which contain OH units (alcohols, glycols, polyols) can be epoxidized by the reaction with epichlorohydrin. These products are used as reactive diluents or flexibilizers for DGEBA resins because of their low viscosities. Aliphatic epoxy resins can be synthesized from different polyolefinic compounds such as unsaturated animal and vegetable oils, polyesters, polyethers and butadiene derived from peracetic acid epoxidation <sup>[41]</sup>.

### 1.2.3 APPLICATIONS OF EPOXY RESINS

Epoxy resins are considered as one of the most important classes of the thermosetting polymer and find extensive use in various fields. The most important application, which has gained their interest is the use of these resins as the matrices for fiber reinforced plastics or composites<sup>[42]</sup>. Some industrial applications are titled below:

- Adhesives<sup>[43]</sup>
- Paints and coatings<sup>[29]</sup>
- Sealants<sup>[44]</sup>
- Electrical system and electronics<sup>[45]</sup>
- Flooring tooling compounds for molds
- Stamping dies and patterns, foams, potting and encapsulation compounds.
- Low-pressure molding resins
- Glass-reinforced plastics<sup>[46]</sup>
- Wear resistance and light emitting diodes<sup>[47]</sup>
- Industrial tooling and composites<sup>[48]</sup>
- Consumer and marine applications<sup>[49]</sup>
- Aerospace, automotive and chemical engineering<sup>[50]</sup>

### 1.2.4 CROSS-LINKING

Cross-linking, a distinctive property of thermosetting polymer, is the covalent bonds formation in which one polymer chain links to another. Crosslinking prevents close packing of the polymer chains, inhibiting the formation of crystalline regions. The extension of the polymer material is restricted by the limited molecular ability of a cross-linked structure. Crosslinks are formed by chemical reactions that are initiated by heat and/or pressure, or by the mixing of an unpolymerized or partially polymerized epoxy resin with specific chemicals called the **cross-linking reagents**<sup>[51]</sup>.

The extent of cross-linking is a measure of the degree of cure. The important properties are obtained at maximum cross-linking. The curing temperature largely influences the ultimate cross-linking density. Heating increases molecular mobility resulting in higher cross-linking density which in turn affects the chemical resistance of the cured matrix. The structure of the hardener has a pronounced effect on the

reactivity and heat resistance of cross-linked epoxy. Aliphatic amines show maximum reaction rate at 90°C while the aromatic amines and phenols react very slowly and require very high cure temperatures <sup>[13]</sup>.

Mostly, cross linking is irreversible, and the resulting thermoset will be destroyed or burnt if heated, without melting. Once a substance is cross-linked, the product is very hard and impossible to recycle.

### **1.2.5 CROSS-LINKING DENSITY**

Crosslinking density is defined as the number of cross-links per volume of the material. The cross link density depends upon the mass of the molecular segments between the cross links and on the ratio of curing agent over the epoxy. Cross-linking density has following effects on resin system properties.

- A low crosslinking density can improve toughness (if strength is not significantly lowered) by allowing greater elongation before breakage.
- A low cross link density can also result in low shrinkage during cure.
- High cross linking density yields an improved resistance to chemical attack.
- Higher cross link density also leads to an increase in the heat distortion temperature (and glass transition temperature), but too high a cross link density lowers the strain to failure (increase brittleness) <sup>[52]</sup>.

### **1.2.6 CURING OF EPOXY RESINS**

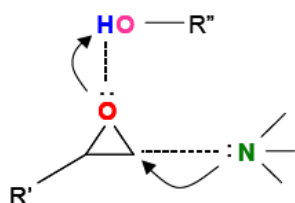
Epoxy resins are reactive intermediate compounds, composed of mixture of intermediate materials containing one or more epoxy groups per molecule. To convert epoxy resins into useful products, they must be cross-linked or cured into three dimensional polymeric networks. Because of ether linkages and cross-linked structure, the resultant product has good dimensional stability, scratch resistance, toughness, chemical resistance, mechanical properties ranging from extreme flexibility to high strength and hardness and high adhesive strength <sup>[53]</sup>. System stability, cure kinetics, resistance and high electrical resistance are influenced by a number of ways. Curing times can be ranged from few seconds to days. The uncured resin can be dry, solid, rubbery or liquid and can cure at temperatures from 5 to 260°C (40–500 °F) depending on the cross-linking agent <sup>[54]</sup>.

Mechanism of epoxy-amine reaction has been studied extensively. The reaction mechanism involves ring opening polymerization of cyclic compound such as epoxides. In the current research, main focus is the reaction mechanism and

kinetics of cross linking reactions of epoxy/amine systems. Shecher was the first person, who proposed “**push-pull**” mechanism for epoxy amine reaction <sup>[55]</sup>. He suggested that the reaction of an epoxide group with an amine occurs through a termolecular intermediate state which contains an epoxide group, an amine and a hydroxyl group. This is a concerted mechanism similar to a bimolecular nucleophilic substitution ( $S_N2$ ) reaction.

Generally the the ring opening polymerization of epoxy group takes place in two conditions: catalytic and autocatalytic.

Rozenberg explained the activations of carbons atoms of the epoxy ring for nucleophilic attack by hydroxyl containing molecule which is identified as “termolecular transition state” <sup>[13]</sup>. The secondary hydroxyl groups catalyse the reaction through termolecular transition state, which facilitate the nucleophilic attack of the amino groups. Thus, as the reaction progresses the cross-linking reaction shows an accelerating rate, which is known as an autocatalytic reaction. Figure 1.11 shows termolecular transition state of epoxy-amine in the presence of hydroxyl containing groups

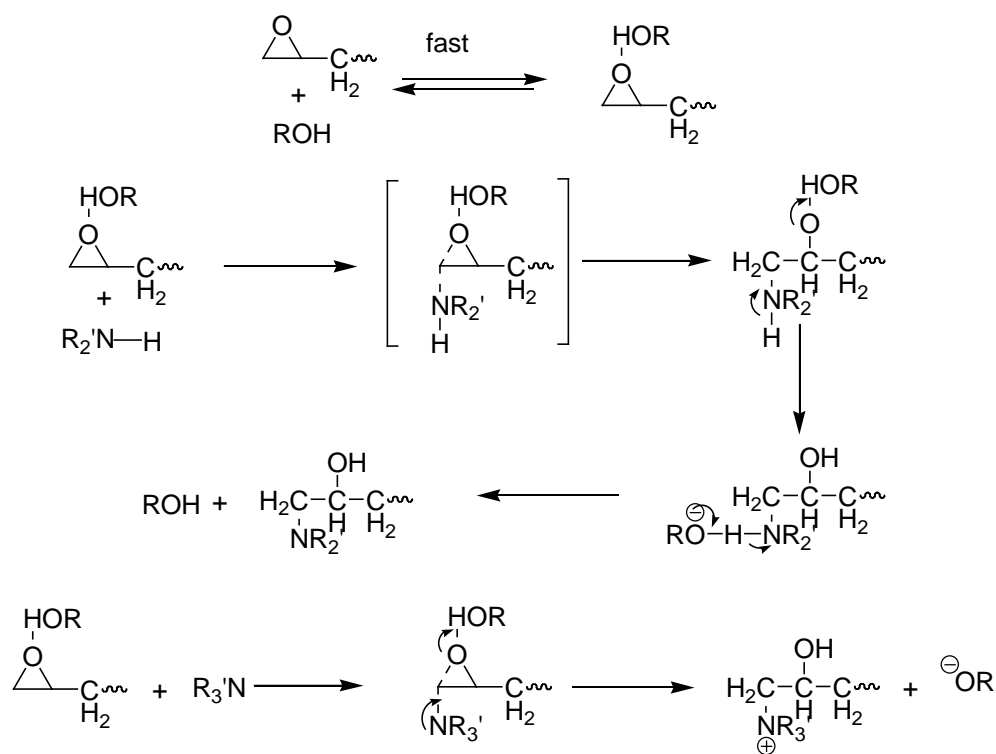


**Fig 1.11: Termolecular transition state of the epoxy-amine addition in the presence of hydroxyl containing groups**

The general mechanism involves a nucleophilic attack of the amine nitrogen on the terminal carbon of the epoxy function. The mechanism has been accepted to be  $S_N2$  type and thus the reaction obeys second order kinetics.

In this mechanism, a primary amine reacts twice with two epoxy group while the secondary amine can react only once with epoxy group. The cross-linking reaction was catalyzed by hydroxyl groups or by catalytic impurities. These will always be present in small amounts upon mixing resins and hardener but may be deliberately introduced through the addition of third component.





**Figure 1.12: Mechanism of epoxy-amine curing** <sup>[56]</sup>

### 1.3 CURING AGENTS (HARDENERS)

Curing agents or hardeners are chemically active compounds which convert epoxy resin into hard, infusible, rigid material. The curing agents play an important role in the curing process of epoxy resin because they affect the curing kinetics, reaction rate, degree of cure, viscosity, cure cycle and final properties of the product.

The choice of resin and hardener depends on a variety of parameters such as type of application, viscosity, pot life, gel time, ultimate mechanical, thermal, chemical and electrical properties, toxicological and environmental limitations and cost <sup>[13]</sup>. The numbers of curing agents have been developed over the years. Epoxy resins can be cured with varieties of functionalities containing active hydrogen such as amine, diaminosulphones <sup>[35]</sup> and anhydrides <sup>[57]</sup> or through esterification of epoxide ring.

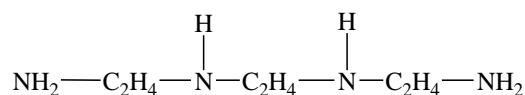
During curing reaction with primary both amino hydrogens can participate in ring opening reactions, thus producing a highly cross-linked structure. Other curing agents may lead to the formation of ester or ether linkages or lead to the catalyzed reaction of alcohol resulting from epoxy ring opening <sup>[58]</sup>.

The cure kinetics and T<sub>g</sub> of cured system depend upon the molecular structure of curing agents. The stoichiometric amount of epoxy-hardener system is important

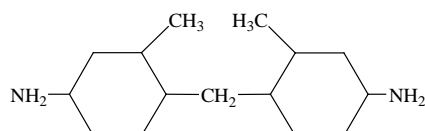
and affects the properties of cured material <sup>[59]</sup>. The amine and phenolic resin based curing agents, extensively used for curing of epoxy resin are described below:

**a) Amine based hardeners**

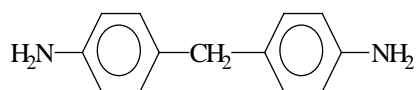
Amines are the most frequently used curing agents. In general, primary and secondary amine are the reactive hardeners, where as tertiary amine are used as catalyst, which are commonly known as accelerators for cure reaction. Diethylenetriamine (DETA) and triethylenetetramine (TETA) are highly reactive primary amines commonly used for room temperature curing of epoxy resins. These diamines have respectively five and six active hydrogen atoms available for cross-linking. Cycloaliphatic amines are found to be increase the pot life e.g., piperidine is shown to be fast reacting and effective in rubber modification of epoxy resins. Aromatic amines react slowly with epoxy resins at room temperature and require high temperature for cure. They give better thermal and chemical resistive properties <sup>[13]</sup>. Some examples of aliphatic and aromatic amine curing agents are shown in figure 1.13.



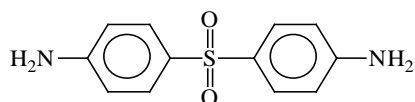
**Triethylenetetra amine**



**2, 2'-Dimethyl-4, 4'-diaminodicyclohexylmethane**



**4,4'-Diaminodiphenylmethane (MDA)**



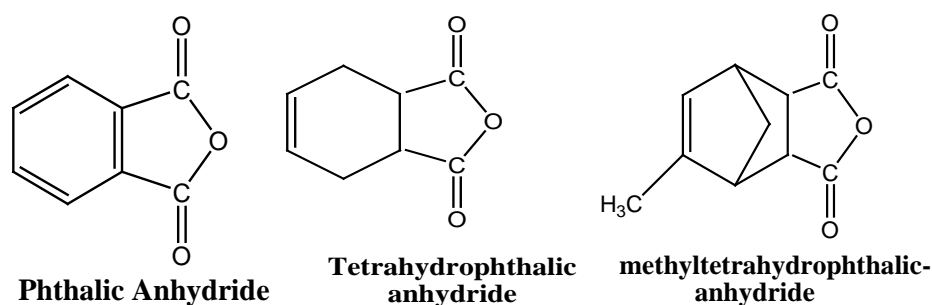
**4,4'-Diaminodiphenylsulphone (DDS)**

**Figure 1.13: Aliphatic and Aromatic Amine curing agents**

Polyamides are the most widely used epoxy hardeners. Primary and secondary aliphatic polyamides give good results at room temperature curing with DGEBA type resins. Polyamides can be used in any ratio with epoxy and they provide mechanical properties, workable pot lives and cure under mild conditions. Paint manufacturers have largely used these resins by esterifying the free hydroxyl groups with unsaturated fatty acids to give a synthetic drying oil <sup>[60]</sup>

### b) Acid/anhydride hardeners

Epoxy resins cured by anhydrides usually have better properties than resins cured by amine and amides. They are less poisonous, display a higher glass transition temperature, and absorb less water, lower exotherms on cure and are less skin sensitive. Practically, anhydrides are preferred to acids since the latter release more water on curing leading to foaming of the product. They exhibit good mechanical and electrical properties. Epoxy-anhydride systems have better thermal stabilities than amine-cured systems. Numerous structurally different anhydrides can be used as curing agents <sup>[61]</sup>. The most important commercial anhydrides are based on a cycloaliphatic structure are shown in figure 1.14.



**Figure 1.14: Important commercial anhydrides**

Phthalic anhydride requires slow curing of epoxies (4-8hours, 150° C) and about 0.6-0.9 equivalent is used per epoxy group. Hexahydrophthalic anhydride is soluble in epoxy resin at ambient temperature and gives higher heat distortion temperatures than phthalic anhydride. Epoxy anhydride systems show low exotherms, long pot life, and little shrinkage upon curing at elevated temperatures. The anhydride hardeners are well-known industrial inhalant allergens, predominantly type I allergies <sup>[62]</sup>.

### c) Miscellaneous curing agents

In addition to amines and anhydrides, many other compounds are also used as curing agents. These include amidoamines, imidazoles, polysulphides, isocyanates

and mercaptanes etc <sup>[63]</sup>. Polyamides are non-irritating amine hardeners and also act as flexibilizers. Dicyanodiamide are also used as curing agent for epoxy resins. Dicyanodiamide (DICY) is insoluble in common resins at room temperature, but dissolves at higher temperatures. Mercaptans gives very high cure rates. Isocyanates react with epoxy group to form oxazolidone structure or on hydroxyl group to form urethane linkages <sup>[13]</sup>.

## **1.4 FILLERS AND REINFORCEMENTS**

Fillers are inert materials which may be organic or inorganic in nature and dispersed in polymeric material. Polymeric material can be filled or reinforced by the addition of inorganic non metallic substances in order to selectively improve certain properties. “Inactive fillers” are called as “extenders” which increases the volume of polymeric material while the “active fillers” improve certain mechanical properties and therefore called as reinforcing fillers. Reinforcement is said to occur if the stiffness and the mechanical strength of the components are higher than the corresponding values of the non reinforced polymer. At the same time, some other properties or even the same property with different direction may be lowered. If the adding component does not lead to reinforcement, but results in lowering of the cost of the final product, although with somewhat poorer mechanical properties, or if it improves the processability, than the adding component is considered as filler.

A necessary condition for a reinforcing effect is that the reinforcing material must have higher strength and higher modulus of elasticity than the matrix. In addition there must be sufficient adhesion between the reinforcing material and the matrix <sup>[64, 65]</sup>.

There are numerous combinations of reinforcements and matrices used to synthesize composite materials. Inorganic particles such as fumed silica or metal-oxide particles mostly affect the mechanical and thermal properties of thermoset polymers. Matrices are combined with nanofillers such as nano-clay <sup>[66]</sup>, silicon dioxide (SiO<sub>2</sub>) <sup>[67]</sup>, titanium dioxide (TiO<sub>2</sub>) <sup>[68]</sup>, zinc oxide (ZnO) <sup>[47]</sup>, Multiwalled carbon nanotubes <sup>[69]</sup>, and alumina (Al<sub>2</sub>O<sub>3</sub>) <sup>[70]</sup>. The properties of composites certainly depend on the particle materials, physical and chemical conditions of their surfaces, the kind of coupling agents to bridge between inorganic and organic substances, and the kind of polymeric material.

## 1.5 NANOTECHNOLOGY

Nanoscience and nanotechnology is considered to be one of the most important future technologies involving several disciplines of science including solid state physics, solid state chemistry, material engineering, medical science and biotechnology. Manipulating matter at nanometer scale, makes it possible to design and create new materials with unprecedented flexibility and novel or improved properties <sup>[71]</sup>.

Nanotechnology is defined as the study of materials and structures having dimensions that measure up to billionth of a meter where unique phenomena enable novel applications. The synthesis of various nanoscale structures has gained the interest in developing new nano materials and devices. For example, the clusters, nanoparticles, nanowires, nanosheets, long molecules as nanotubes and polynucleotides, and functional supra-molecular nanostructures are currently considered as potential building blocks for nanotechnology and nanoelectronic devices and circuits. The properties of many conventional materials change when they are in nanoparticles form. This is because nanoparticles have a greater surface area per weight than larger particles; this causes them to be more reactive to certain other molecules.

Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures <sup>[72]</sup>. When the size of the material reaches up to the level of nanometric scale, many atoms become part of the crystallite surface, rather than being fully bonded ‘‘bulk’’ atoms <sup>[73]</sup>. A bulk material should have constant physical properties regardless of its size, but as the size of the material reaches to the nano-scale size-dependent properties are often observed. For a bulk material, when dimensions are larger than one micrometer, the percentage of atoms at the surface is insignificant as compared to the number of atoms in the bulk of the material <sup>[74]</sup>.

Atoms present at the surface are distinguished by their reduced coordination to the crystal backbone. They are more able to react with neighboring atoms or to exhibit other unusual physical or chemical properties. Surface atoms play an important role in the thermodynamic characteristics of solids, particularly in the case of nanoparticles where such atoms determine structural transitions. The specific heats of phase transition, conductance, magnetic susceptibility, and other fundamental physical

characteristics are drastically changed when the particles reached to the nanoscale size. It is also worth noting that other physical characteristics such as the melting point of crystallites, the pressure needed for crystalline structure rearrangement, ionization potentials, bond energies, intra atomic distances, optical and magnetic properties, etc. essentially changed as the particle size continues to decrease within the nanoscale range <sup>[73]</sup>.

### 1.5.1 NANOCOMPOSITES

Nanocomposite is a class of materials with unique physical properties and wide applications in diverse areas <sup>[75]</sup>. Nanocomposites refer to the composites of materials consisting of more than one solid phase where at least one of the components has a dimension in the nanometer range. The solid phases may be inorganic or organic, or both, with amorphous, semi-crystalline or crystalline phase or combinations of these phases <sup>[71]</sup>.

Polymer nanocomposites are an important class of polymers that have wide range of applications due to their improved thermo-mechanical properties, gas barrier performance, improved thermal properties, and greatly reduced flammability and, thus, organic/inorganic nanocomposite materials have been extensively studied in recent decades <sup>[70]</sup>. Depending upon the dimensions of the dispersed particles in the nanometer range, nanomaterials are classified into three categories; nanoparticles, nanotubes and nanolayers. Inorganic nanoscale fillers, include layered silicates (such as montmorillonite), nanotubes (mainly carbon nanotubes, CNTs), fullerenes, SiO<sub>2</sub>, metal oxides (e.g., TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, ZnO), nanoparticles of metals (e.g., Au, Ag), polyhedral oligomeric silsesquioxane (POSS), semiconductors (e.g., PbS, CdS), carbon black, nanodiamonds, etc. All these nanoparticles are used in order to enhance physical, mechanical and chemical properties. Nanoparticles can also enhance flame retardancy and thermal degradation of nanocomposites. As the demand for non-halogenated flame retardant additives for polymeric end products is increasing, they gained much importance in recent years. Thus, the nanoscale reinforcement of polymers is becoming an attractive way to improve the thermal stability of polymers <sup>[76]</sup>.

Homogenous dispersion of nanoparticles in polymeric matrix is a key factor in preparation of polymeric nanocomposites. The unique properties of nanocomposites are mainly due higher surface area of the nanosized particles in comparison to

microsized fillers caused by their large surface area to volume ratio [77]. Nanocomposites differ from both pure polymers and inorganic fillers in some physical and chemical properties [75]. The surface to volume ratio at nano level is large and thus the inorganic nano-material is expected to refine mechanical, thermal, biological, magnetic, optical, electronic, optoelectronic, and electrical properties compared with conventional composites. By incorporating only a little amount of nanoparticles into polymer matrix interesting optical properties including absorption, fluorescence, luminescence, nonlinearity, high reflex index (RI), magnetic properties, and excellent mechanical properties may be obtained [71].

Inorganic fillers are known to affect the cure kinetics of thermosetting polymers. They can change the network structure of polymer and affect the kinetics of the epoxy resin. An alternative way to increase the toughness of the matrix and to improve some of its properties can be done by the introduction of rigid inorganic particles. Commonly, inorganic fillers are inexpensive and reduce the cost of the final product. The principal role of most inert inorganic fillers is to occupy volume in a film [43].

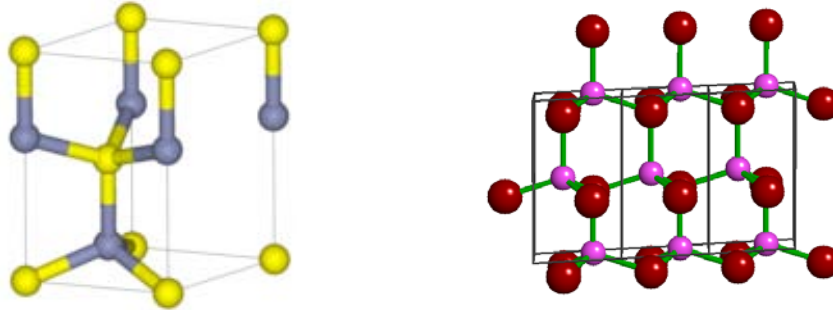
Inorganic nanoparticles/ polymer nanocomposites are prepared by three general ways. The first method involves direct mixing of the polymer and the nanoparticles either as discrete phases or in solution. In second method in-situ polymerization in the presence of the nanoparticles or the *in-situ* formation of nanoparticles in a polymer matrix is done while in third method both *in-situ* formation of the nanoparticles and polymerization is carried out.

## 1.6 ZINC OXIDE

Zinc oxide is an inorganic compound with the formula ZnO formed from a  $\text{Zn}^{+2}$  cation and  $\text{O}^{-2}$  as anion. It is commonly called as *Zincite* which rarely occurs in nature. Most of the commercially used ZnO is produced synthetically. It is a white crystalline powder which is insoluble in water [78].

ZnO is referred as II-VI compound, since  $_{30}\text{Zn}$  is a group IIb element and  $_{8}\text{O}$  is a group IV element of periodic table. Zinc has five stable isotopes. The prevalent ones are  $_{64}\text{Zn}$ (48.89%)  $_{66}\text{Zn}$ (27.81%) and  $_{68}\text{Zn}$ (18.57%) while oxygen almost purely exists in the form of  $_{16}\text{O}$ (99.76%). Zn has electronic configuration  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}$  and the configuration of oxygen is  $1s^2, 2s^2, 2p^4$  [79].

ZnO in its crystal lattice involves  $sp^3$  hybridization of the electron states, leading to four equivalent orbitals, directed in the tetrahedral geometry. The tetrahedral geometry determines the crystal structure of ZnO illustrated in figure 1.15. Each zinc ion is surrounded by four oxygen ions in a tetrahedral configuration and vice versa <sup>[80]</sup>.



**Figure 1.15: Tetrahedral structure of ZnO**

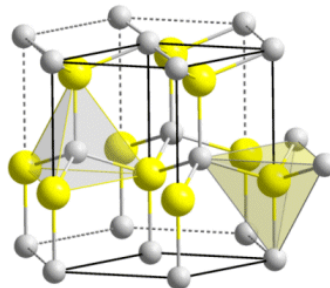
### 1.6.1 CRYSTAL STRUCTURE

Zinc oxide exists in two crystalline forms.

- Hexagonal wurtzite.
- Cubic structure.

#### 1) Hexagonal wurtzite

Hexagonal wurtzite is the most stable structure at ambient conditions and thus the most common. ZnO has hexagonal close packed braves lattice. The number of nearest neighbors in hexagonal wurtzite is four. Each O (or zinc) ion is tetrahedrally surrounded by four zinc (or O) ion. Each ion also has twelve next nearest neighbors of the same type of the ion <sup>[79]</sup>.

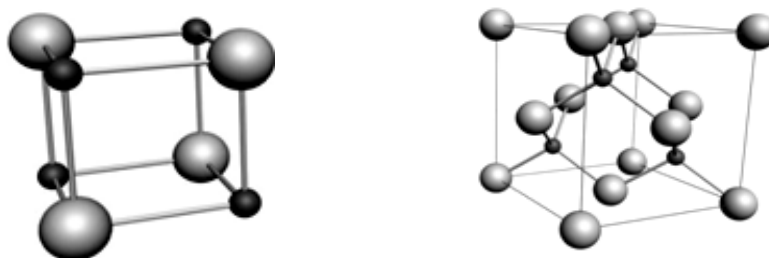


**Figure 1.16: Hexagonal wurtzite structure of ZnO**



## 2) Cubic structure

Cubic structure either has a zinc blende or rocksalt morphology. The zinc blende ZnO structure can be stabilized only by growth on cubic structure, and the rocksalt structure (NaCl) can be obtained at relatively high pressure. Under normal conditions, hexagonal wurtzite ZnO is thermodynamically stable and at pressures of about 9 GPa and room temperature transforms into the cubic modification <sup>[78]</sup>.



**Figure 1.17: Rock salt and zinc blende structure of ZnO phases**

### 1.6.2 PROPERTIES OF ZnO NANOPARTICLES

ZnO bulk material is a wide band gap semiconductor and exhibits distinct optical and electronic properties. In comparison to the bulk materials, low scale nanoscale materials with their large surface areas and possible quantum confinements effects, exhibits different electronic, optical, chemical and thermal properties <sup>[81]</sup>. The properties of ZnO nanomaterials are discussed below:

#### a) Mechanical Properties

ZnO is a relatively soft material with approximate hardness of 4.5. Due to high heat capacity and heat conductivity, low thermal expansion and high melting point, ZnO are beneficial for ceramics <sup>[78]</sup>.

#### b) Electrical Conductivity

In its normal form, zinc oxide is an n type semiconductor, and conducts electricity by electrons. This conductivity might be due to a stoichiometric excess of zinc ions which occupy interstitial locations in the crystal lattice. ZnO has a wide band gap of 3.3 eV. Several advantages associated with a large band gap include higher breakdown voltages, ability to sustain large electric fields, lower electronic noise, and high-temperature and high-power operation <sup>[82]</sup>.

### **c) Optical properties**

Nanosized ZnO is a semiconductor, has an absorption edge at a wavelength of about 380 nm and can shield most of ultraviolet-A (UVA) and ultraviolet-B (UVB) rays. Due to smaller refractive index (2.0) than other metal oxides (for example, titanium dioxide: 2.4–2.7), ZnO nanoparticles have simultaneous high-visible light transparency and high-UV light shielding efficiency, showing great potential as UV-shielding materials in resin, UV-protecting coatings, transparent UV-shielding inorganic-polymer nanocomposites, and sunscreen cosmetics <sup>[83]</sup>.

Active species are released when photocatalytic active ZnO absorbs light energy equal to or greater than its band gap energy, facilitating degradation of organic compounds and hindering the practical application of ZnO as an UV-blocking material. It is therefore imperative to prepare ZnO that has suppressed surface activity and high UV-shielding ability in some practical applications <sup>[84]</sup>.

### **d) Piezoelectric properties**

Piezoelectricity is the mechanism of converting mechanical energy into electrical energy and vice versa. Direct piezoelectrical effect is referred to the generation of electrical polarization when piezoelectrical material is strained. ZnO has been used for several piezoelectric devices since the early 1970's, due to its moderate coupling coefficient and ease of deposition. Due to lack of center of symmetry, ZnO combines with large electromechanical coupling, result in strong piezoelectric and pyroelectric properties and a consequent use of piezoelectric sensors, piezoelectric diodes and nanogenerators <sup>[85, 86]</sup>.

## **1.7.3 APPLICATIONS OF ZINC OXIDE NANOPARTICLES**

Nanocrystalline semiconductor materials have attracted a great deal of attention to the researchers for both their fundamental size and shape dependent physiochemical properties and potential applications in numerous areas. ZnO nanoparticles have attracted much interest because of various remarkable chemical and physical properties which are distinct from conventional bulk material.

ZnO is a semiconductor material and used in solar cell windows, light emitting diodes (LED), piezoelectric appliances, varistors, gas sensors, electroluminescent, devices, photosensitization, field emission display, UV photodetectors, and transducers <sup>[87]</sup>. It is also a promising candidate for nanoelectronic and photonics <sup>[88]</sup>.

Due to its UV absorbing capability, it is used in bright green luminescence phosphor in fluorescent devices <sup>[89]</sup>, room temperature UV-lasers, catalysts, transparent conducting films, ultraviolet-protection films, <sup>[90]</sup> sunblocks, cosmetic, creams, ointments and lotions formulations <sup>[91]</sup>.

ZnO NPs are nontoxic, biosafe, and biocompatible and have been used in many applications in daily life, such as drug carriers and in cosmetics and fillings in medical materials, biosensors, biogenerators, bioelectrodes <sup>[92]</sup>.

#### **1.6.4 SYNTHESIS OF ZnO NPs BY CO-PRECIPITATION METHOD**

ZnO nanoparticles have attracted much interest because of their various remarkable chemical and physical properties that are distinctive from those of conventional bulk materials. Many different synthesis routes for the production routes of ZnO Crystallites with different morphologies have been established. Various methods have been adopted for the preparation of ZnO crystallites including sol–gel method, evaporative decomposition of solutions, gas-phase reaction, wet chemical synthesis and hydrothermal discharging gas method spray pyrolysis, sputtering, vapour–liquid–solid growth, and physical vapour deposition, thermal decomposition <sup>[93]</sup>. A large number of the reported techniques involve elaborate, time-consuming steps, long reaction times, high temperatures, complicated processes and/or the use of toxic precursors, which might result in impurities in the final products. However, in order to obtain ZnO nanocrystals with appropriate chemical and optical properties for their intended applications, control of morphology, chemical composition, purity and particle size during synthesis are very important. Several studies have demonstrated that a coprecipitation process has many advantages over the others in order to obtain highly crystallized nano-powders with a narrow grain size distribution, high purity and low calcination temperature. Specifically, the particle properties of ZnO, such as crystallinity and morphology, can be controlled by adjusting factors such as the precursors, pH value, reaction temperature, time, and so on <sup>[89, 94]</sup>.

When precipitates are separated out from solution, they may not be perfectly pure. The contamination of a precipitate by a substance which is normally soluble in mother liquor is generally termed as co-precipitation. It is concerned with adsorption at a particle surface when exposed to the solution and occlusion of foreign substances during the process of crystal growth from primary particles. The longer the time of

contact the greater will be the precipitation which generally occurs on the surface of first precipitate <sup>[95]</sup>.

One drawback of coprecipitation method is the difficulty controlling the particle size and morphology. This is the result of chemical reaction in aqueous solution being very rapid. One possible way to control the particle size and morphology during the synthesis of nanoparticles is the use of capping agents or surfactants <sup>[94]</sup>.

### **1.6.5 CAPPING AGENT/ SURFACTANT**

Capping agent is a strongly absorbed monolayer of usually organic molecules used to aid stabilization of nanoparticles. Capping agents play a key role in controlling the morphology and shape of nanoparticles. Amine, long chain alkanes, fatty acids and thiol based surfactants are used to control the morphology of particles <sup>[96]</sup>.

As the nuclei grow, van der Waals interactions can cause rapid coalescence of nuclei and an unrestrained nanoparticles growth. However, addition of the capping agent during synthesis limits the particle-particle aggregation.

Capping agent/surfactant-assisted synthesis has been widely explored for fabrication of nanorods, nanotubes and other complex nanostructures, The surfactant molecules absorb and desorb rapidly from the surface of nanocrystals at the growth temperatures, enabling the addition and removal of atoms from the crystallites, and aggregation is suppressed by the presence of one monolayer of surfactant at the crystallite surface <sup>[97]</sup>.

The nature and amount of organic surface capping agents used have been found to be crucially important for nanostructure fabrications. The synthesis of almost all nanocrystals is in reality carried out in the presence of a capping agent to stabilize the desired size for a given application. In some cases capping agent also play a role in influencing the kinetics of the chemical processes involved.

## **1.7 LITERATURE REVIEW**

In the last decade nanocomposite materials, consisting of a polymeric matrix materials and nanofillers have attracted scientific and industrial interest due to their enhanced properties. They exhibit superior property enhancements at a low filler contents as compared with the conventional micro and macro- or neat counterparts <sup>[98]</sup>. Metallic oxides nanoparticles have useful properties and characteristics that are

crucial for many applications; among them high electric conductivity, paramagnetism, high thermal conductivity as well as good mechanical properties are the most important ones. Combination of polymer and nanoparticles has enhanced electrical magnetic and thermal properties comparable with the properties of metals <sup>[99]</sup>.

Following is a review of some work reported in the literature on the effects of introducing zinc oxide nanoparticles in a polymer matrix:

Nano ZnO with neoprene rubber was studied by Begum et al. apparently addition of a lower percentage of ZnO was sufficient for improving mechanical properties of the compound.

Transparent ZnO/epoxy nanocomposites with high-UV shielding efficiency were reported by Li and co-workers <sup>[83]</sup>. Transparent ZnO/epoxy nanocomposites were prepared from transparent epoxy (EP-400) and as-synthesized ZnO nanoparticles via in situ polymerization. The nanocomposite containing a very low content (0.07% in weight) of ZnO nanoparticles with an average particle size of 26.7 nm after calcination at 350 °C possessed the most optimal optical properties, i.e., high-visible light transparency and high-UV light shielding efficiency that are desirable for many important applications.

The curing, thermal degradation kinetics and mechanical properties of epoxy resin based on the diglycidylether of bisphenol A, 2,2-Diamino-1,1-binaphthalene as a hardener and ZnO as a nanofiller were investigated by Zabihi and his colleagues <sup>[43]</sup>. They obtained higher thermal and mechanical properties with 5% of ZnO nanoparticles. The addition of ZnO nanoparticles into the epoxy matrix resulted in a significant increase in the thermal stability and activation energy of thermal degradation. The epoxy nanocomposite exhibited an increment in storage modulus and glass transition temperature compared to the neat epoxy.

Carri'on et al. have synthesized polycarbonate (PC)/zinc oxide (ZnO) nanocomposites containing 0.1, 0.5, 1 or 5 wt.% nanoparticles by milling and injection molding <sup>[100]</sup>. They investigated that increasing the concentration of ZnO nanoparticles reduces the glass transition temperature and the degradation temperature of the nanocomposites with respect to neat PC. The nanocomposites containing 0.5% and 1% wt. ZnO were selected for mechanical and tribological studies. PC with 0.5% ZnO presented a higher modulus and similar tensile strength compared to neat PC, with a 74% reduction in the elongation at break. ZnO concentration of 1 wt.% dramatically reduced both the tensile strength and the elongation at break of PC. 0.5

wt.% proportion of ZnO nanoparticles increased hardness and reduced the wear rate with respect to neat PC both under pin-on-disk and under thrust-washer contact conditions.

The effects of particle size of zinc oxide (ZnO) on mechanical, thermal and morphological properties of pure polyoxymethylene (POM) and POM/ZnO nanocomposites were investigated by Wacharawichanant and co-workers <sup>[101]</sup>. They prepared POM/ ZnO nanocomposites with varying concentration of ZnO by a melt mixing technique in a twin screw extruder. The POM/ ZnO71 (71nm) and POM/ ZnO250 (250 nm) nanocomposites showed decrease in tensile strength with increasing filler content. Young's modulus and stress at break increased with increasing filler contents. The strength of POM nanocomposites increased up to a ZnO content of 1.0 wt%. Similarly, the mechanical properties and degradation temperature of POM/ ZnO71 nanocomposites were higher than the POM/ ZnO250 nanocomposites.

Huang et al adopted sol-gel chemical route to prepare the zinc oxide (ZnO) nanoparticles as small as 4 nm. UV-curable ZnO-acrylic nanocomposites were prepared by employing 3-(trimethoxysilyl)propyl methacrylate (TPMA) as the surface modification agent of ZnO particles. UV-Vis analysis revealed a high optical transparency (>95%) in visible light region for nanocomposites films with ZnO contents up to 20 wt%. The addition of ZnO nanoparticles also enhanced the dielectric constants of nanocomposites <sup>[102]</sup>.

Most of the studies relating to transparent nanocomposites mainly focused on the optical applications. For instance, transparent ZnO-epoxy nanocomposites have been prepared by Yang et al. and applied to the encapsulation of solid-state lighting devices <sup>[103]</sup>.

Liufu et al. investigated the thermal degradation behavior of polyacrylate and its zinc oxide composites <sup>[104]</sup>. He studied that filler-free polyacrylate exhibited one TGA peak, indicating that the polymer was degraded with only one stage of weight loss while Polyacrylate/ZnO composites underwent two minor weight losses as well as the major weight loss. Kinetics of thermal degradation of filler-free polyacrylate and polyacrylate/ZnO composite were quantitatively obtained by means of non-isothermal weight loss data analysis.

The mechanical and viscoelastic properties of an epoxy-polyamide coating containing nano and micro sized ZnO particles were studied by Ramezanzadeh and

Attar <sup>[105]</sup>. They prepared nanocomposites with different loadings of the nano sized ZnO particles.  $T_g$  and cross- linking density of the composites were decreased using nanosized ZnO particles as well as the Young's modulus and the fracture energy of the coating. The greater toughness as well as fracture energy of the composite was obtained when it was reinforced with the nanosized ZnO particles.

Nanocomposites made of ZnO nanoparticles dispersed in thermoplastic polyurethane were synthesized by Wagener and co-workers using picosecond laser ablation of zinc in a polymer-doped solution of tetrahydrofuran <sup>[106]</sup>. These nanocomposites showed a green photoluminescence emission centered at 538nm after excitation at 350 nm, which should be attributed to oxygen defects generated during the laser formation mechanism of the monocrystalline nanoparticles. They also investigated the influence of pulse energy and polymer concentration on the production rate, laser fluence and energy-specific mass productivity.

New dispersions of the ionic liquid (IL) 1-octyl-3-methylimidazolium tetrafluoroborate ([OMIM]BF<sub>4</sub>) and ZnO nanoparticles in epoxy resin have been prepared by Sanes et al <sup>[107]</sup>. The presence of ZnO nanoparticles increases the stiffness of the epoxy resin, while the addition of the ionic liquid (IL) enhances chain mobility and produces a plasticizing effect.

Ding, Wang and Zhang prepared ZnO/epoxy composites with homogeneous dispersion via *in-situ* preparation of zinc hydroxide (Zn(OH)<sub>2</sub>)/ epoxy from the reaction of aqueous zinc acetate (Zn(Ac)<sub>2</sub>.2H<sub>2</sub>O) and sodium hydroxide (NaOH) at 30 °C in the presence of high viscosity epoxy resin <sup>[47]</sup>. Compared to pure epoxy resin, the improvement of ultimate tensile stress, elongation at break, tensile modulus and flexural strength were achieved by about 40.84%, 24.35%, 27.27% and 51.43% by the addition of ZnO respectively.

Transparent inorganic UV-filter/epoxy nanocomposites with high photo-stabilization properties were reported by Li et al <sup>[108]</sup>. He subsequently prepared transparent inorganic UV-filter/epoxy (ZnO/epoxy, S-T/epoxy and S-T-S/epoxy) nanocomposites from the transparent epoxy and the as-prepared nanoparticles via *in situ* polymerization method. The results showed that the photo-stabilization effect of inorganic UV-filter on the lifetime of LED lamp obeys the following sequence: ZnO > S-T-S > S-T. By comparing the UV LED lamps encapsulated with pure epoxy, the lifetime of UV LED lamps encapsulated with ZnO/epoxy, S-T-S/epoxy and S-T/epoxy nanocomposites has been improved by 76%, 54% and 33%, respectively.

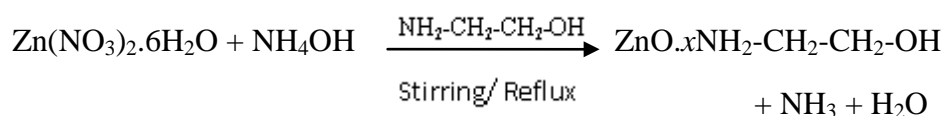
## 1.8 PLAN OF WORK

A lot of work on ZnO-epoxy has already been done but the objective of present research work is to synthesize ZnO epoxy amine nanocomposites by varying the size and percentage of ZnO nanoparticles and to check the optical, thermal and mechanical properties. Surface functionalized ZnO nanoparticles were synthesized which were incorporated into organic polymer. The epoxy used for this purpose is diglycidyl ether of Bisphenol A abbreviated as DGEBA (DER332) and the diamine used was 2,2'-Dimethyl-4,4'-diaminodicyclohexylmethane (MACM). The particulate reinforcement was synthesized by co-precipitation method using a new procedure. In this method  $Zn(NO_3)_2 \cdot 6H_2O$  was used as precursor and 2-aminoethanol was taken as solvent as well as capping agent. This capping agent enhances the interaction between nanoparticles and polymer matrix.

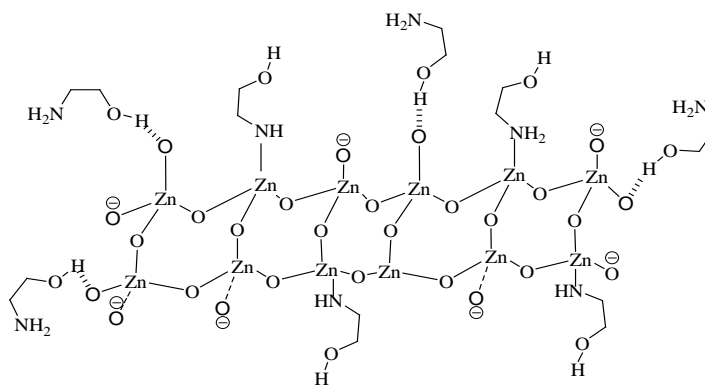
The present research work was divided into two parts. The first portion includes synthesis of ZnO nanoparticles while the second portion includes incorporation of these nanoparticles into epoxy amine matrix to synthesize epoxy-amine ZnO nanocomposites.

### a) Synthesis of ZnO nanoparticles

In present work,  $NH_4OH$  was added in  $Zn(NO_3)_2 \cdot 6H_2O$  solution. The overall reaction can be written as:



Co-precipitation method was used for the synthesis of nanoparticles.



**Figure 1.18: Schematic representation of surface functionalized ZnO nanoparticles**

These surface functionalized ZnO nanoparticles were characterized by UV, FTIR, XRD, PL, TGA & SEM.



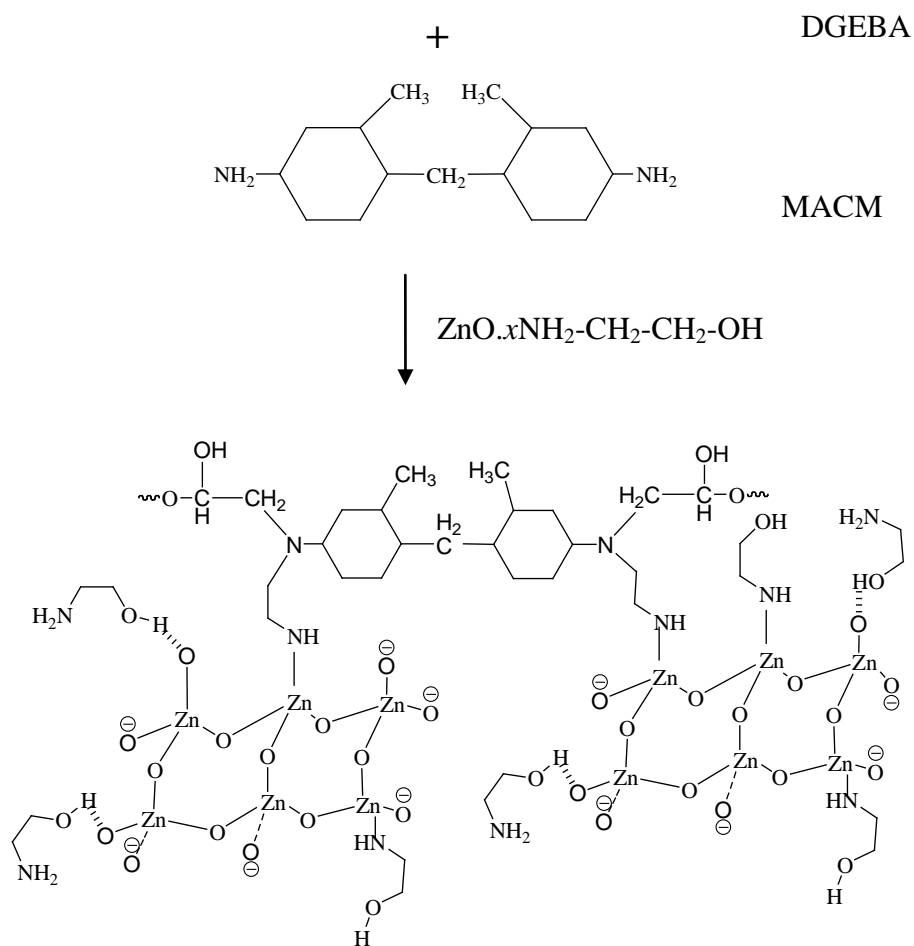
## **b) Synthesis of epoxy-amine ZnO nanocomposites**

When using a two component epoxy-amine system, the bonding process starts out by mixing the two components. The difunctional epoxy resin i.e., DGEBA reacts with the diamine i.e., MACM to form an extended, durable three dimensional network.

When surface functionalized ZnO nanoparticles are introduced into epoxy-amine network, the interaction between polymer and nanoparticles takes place. This interaction may be in the form of Van der Waal intermolecular forces or due to a covalent bond formation <sup>[109]</sup>.

The properties of the composite systems were studied as a function of the type of the filler used. Also the epoxy-amine-ZnO nanocomposites were synthesized by using various sizes and percentages of reinforcement. Thus two particles size were selected for composites synthesis. These two differently sized particles were either calcined or un-calcined. ZnO nanoparticles were calcined at 300°C. In nanocomposites it was expected that both particle and epoxy were attached with MACM.

Thus four types of series were synthesized. The composites were characterized by SEM, XRD, DSC and FT-IR.



**Figure 1.19: A general scheme showing probable reaction of Epoxy- amine ZnO network**

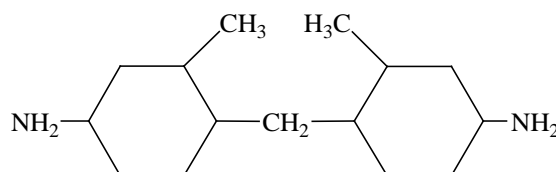
This chapter describes in detail the chemicals used, the procedures adapted for the synthesis of various sized ZnO nanoparticles and characterization techniques used for the analysis of ZnO particles and epoxy-amine–ZnO nanocomposites.

## 2.1 CHEMICALS USED

The liquid epoxy of the type, diglycidyl ether of bisphenol A, DGEBA (DER - 332) was obtained from DOW chemicals and was used as received. It has molar mass of 348.52g/mol, the equivalent weight per unfunctional group is  $E_E = 174.26$  g/mol and value of polydispersity index ( $n$ ) is 0.03.

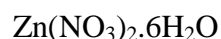
**Figure 2.1: Diglycidyl ether of bisphenol A DGEBA (DER-332)  $n = 0.03$**

2,2'-Dimethyl-4,4'-diaminodicyclohexylmethane (MACM) was available commercially. It has molar mass of 238.41g/mol, the equivalent weight per functional group is 59.60g/mol.



**Figure 2.2: 2, 2'-Dimethyl-4,4'-diaminodicyclohexylmethane**

Zinc nitrate hexahydrate was obtained from Sigma Aldrich and was used as received. Its molar mass is 297.49 g/mol and its m.p is 36.4°C.



**Figure 2.3: Zinc nitrate hexahydrate**

2-Aminoethanol was obtained from Fluka. Its molar mass is 59g/mol and its b.p is 170°C. Ammonium hydroxide 33% was obtained from Lab-Scan and was used as received. Its molar mass is 35.04g/mol and its b.p is 24.7°C.

### **2.1.1 SOLVENT USED**

Ethanol was dried on CaO for 6 hours and then distilled <sup>[110]</sup>.

## **2.2 CHARACTERIZATION TECHNIQUES**

### **2.2.1 FOURIER TRANSFORM INFRA-RED SPECTROSCOPY (FTIR)**

The solid state fourier transform infrared spectra (4000-400  $\text{cm}^{-1}$ ) were recorded on THERMO SCIENTIFIC NICOLET 6700 instrument.

### **2.2.2 X-RAY DIFFRACTION ANALYSIS (XRD)**

X-ray diffraction analysis was carried out at 25° C using Siemens d 5000 X-ray instrument using Cu K alpha radiation.

### **2.2.3 ULTRA-VIOLET SPECTROSCOPY (UV-vis)**

Ultra-violet visible spectroscopy was carried out at 25°C by using SCHIMADZU spectrophotometer, Model Pharma spec UV-1700. The cuvetts used are made up of quartz by SCHIMADZU.

### **2.2.5 DIFFERENTIAL SCANNING CALORIMETRY (DSC)**

DSC was carried out with METTLER TOLEDO 823C DSC instrument. 7-8 mg of sample was heated in a sealed aluminum pan from 0°C- 350°C at a heating rate of 10° C/min, under nitrogen atmosphere.

### **2.2.6 THERMOGRAVIMETRIC ANALYSIS (TGA)**

Thermogravimetric analysis was carried out with METTLER TOLEDO TGA/DSC analyzer 851C at 25°C. 7-8 mg of sample was heated to 700°C under air atmosphere at the heating rate of 10°C/min.

### **2.2.7 SCANNING ELECTRON MICROSCOPY (SEM)**

Scanning electron microscopic analysis of composite films was done at 25°C using Jeol, JFM 5910, SEM analyzer manufactured by Japan.

## 2.3 EXPERIMENTAL

The experimental work consisted of two parts. The first part includes the synthesis of ZnO nanoparticles and in second part, composites films were synthesized by using these ZnO nanoparticles.

ZnO nanoparticles of variable sizes were synthesized by coprecipitation method, using  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  by varying time and temperature of the reaction. 2-aminoethanol was used as solvent as well as capping agent. From the range of different sized particles obtained, only two sizes were selected for incorporation into composites films.

Using above mentioned ZnO nanoparticles i.e. 35 & 40 nm, four types of organic-inorganic systems were synthesized using DGEBA and MACM.

1. Composite system using diamine MACM as hardener, reinforced with uncalcined ZnO nanoparticles obtained after 15 minutes of reflux (TTN 01).
2. Composite system using diamine MACM as hardener, reinforced with calcined ZnO nanoparticles obtained after 15 minutes of reflux (TTN 02).
3. Composite system using diamine MACM as hardener, reinforced with uncalcined ZnO nanoparticles obtained after 30 minutes of reflux (TTN 03).
4. Composite system using diamine MACM as hardener, reinforced with calcined ZnO nanoparticles obtained after 30 minutes of reflux (TTN 04).
5. In addition, a neat matrix was also prepared by using DGEBA and MACM only in a stoichiometric ratio of amino hydrogen to epoxy equal to one.

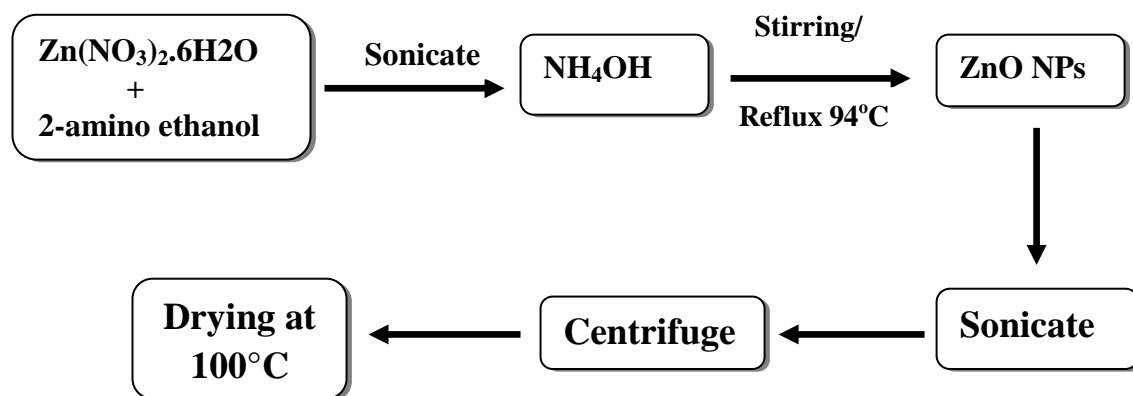
In all these series percentage of ZnO nanoparticles varied from 0.5% to 2.0%. All compositions were analyzed by UV, IR, SEM, XRD and DSC.

### 2.3.1 SYNTHESIS OF ZnO NANOPARTICLES

ZnO nanoparticles with variable fine particle size were synthesized by precipitation method. Zinc nitrate hexahydrated was used as precursor. By varying the time and temperature of the reaction, the particle size was tuned from 9 nm to 70 nm. Hexagonal wurtzite crystal structure was obtained by using 2-aminoethanol. It was used as solvent as well as capping agent/surfactant. Capping agent/surfactant can alter the relative growth rate in different crystallographic planes due to its adsorption on some specific planes of the growing ZnO nanoparticles<sup>[88]</sup>.

### 2.3.1.1 PROCEDURE

20 mL of 2-aminoethanol was taken in 500mL round bottom flask. 14 mmol (4.15g) of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was added in it and was dissolved through sonication. Then 10 mL of  $\text{NH}_4\text{OH}$  was added and the solution was diluted with distilled water to make the pH of 11.2. Different series of reaction were performed either by varying the time or temperature of the reaction. In temperature varying series, the reaction was carried out by stirring at room temperature or by refluxing at  $94^\circ\text{C}$  for variable time periods i.e., for 15 min, 30 min, 60 min and 120 min as described in the table 2.1. White precipitates of ZnO nanoparticles were formed. Solvent was decanted off from synthesized particles. The particles were sonicated for 1 hr in ethanol. The product was then washed with distilled water three times and solid particles were recovered by centrifugation. Finally the product was dried in an oven at  $100^\circ\text{C}$ . The as-synthesized ZnO was analyzed by UV, IR, SEM and XRD. Surface functionalized ZnO particles were confirmed through IR and TGA. Figure 2.4 shows a schematic representation of this procedure.



**Fig 2.4: Schematic representation showing synthesis of uncalcined ZnO nanoparticles.**

In order to calcined, the as-synthesized ZnO nanoparticles were kept in open air furnace at  $300^\circ$  for 3 hours.

**Table 2.1: Variation in time and temperature for synthesis of ZnO**

Growth time min	Temperature of reaction (°C)	Particle size nm	Physical state	Sample codes
320	60	14.88	White powder	TE 01
320	60	16.10		Uncalcined TE 02 Calcined*
15	60	9.80	White powder	TE 03
30		15.26		TE 04
60		10.66		TE 05
120		12.50		TE 06
-	70	33.82	White powder	TE 25
-	75	40.28		TE 26
-	80	43.15		TE 27
15	94	35.62	White powder	TE 20
30		40.28		TE 21
60		65.40		TE 22
120		69.50		TE 23

\*Calcined at 300°C

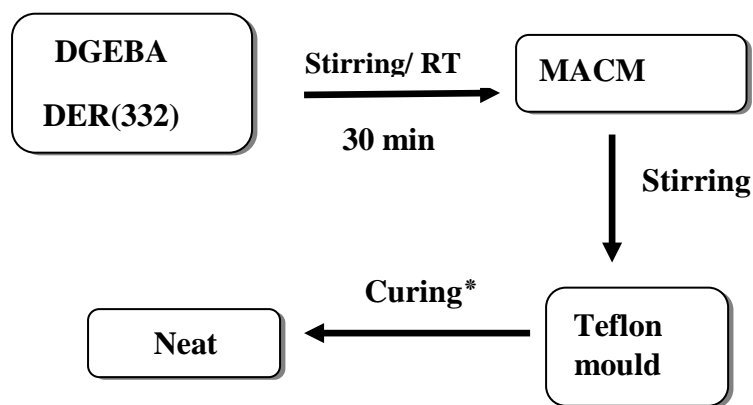
### 2.3.2 SYNTHESIS OF COMPOSITES

Epoxy-amine-ZnO nanocomposites were synthesized using MACM (3,3'-dimethyl-4,4'-diaminodicyclohexylmethane) as a hardener. For comparison purpose a neat matrix was synthesized and abbreviated as TN-neat.

#### 2.3.2.1 SYNTHESIS OF NEAT EPOXY-AMINE NETWORK (TN-NEAT)

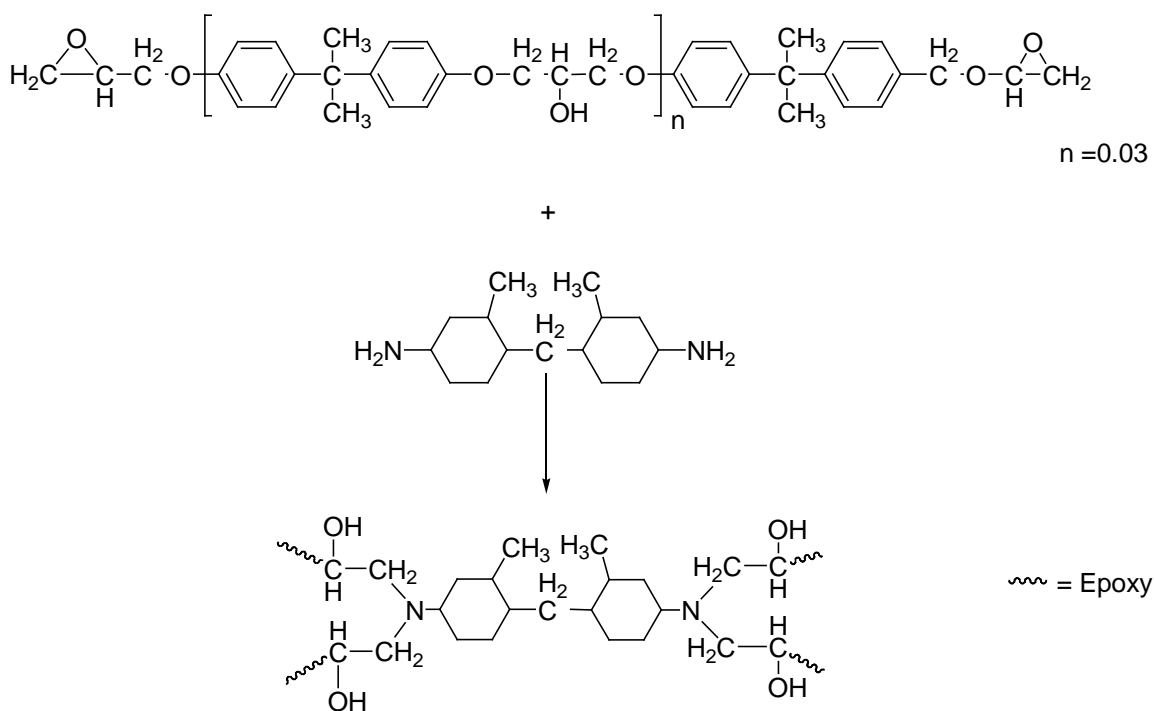
For this purpose weighed amount of DGEBA i.e., 1.49g (57 mmol) was taken in a 30mL beaker. It was vigorously stirred for half an hour allowed to melt at room temperature. During this period the mixture was degassed for 10 minutes, in a vacuum oven to remove air bubbles. Finally 0.50 g (2.0 mmol) MACM was added and stirred for 20 minutes.

Stoichiometric amounts of amino hydrogen to epoxy equal to 1. Controlled thickness was achieved by casting the measured amount of reaction mixture in the moulds and then placing the moulds on a plane surface in the oven at 50°C for 1 hour, 60°C for 1hour, 70°C for 1 hour, and 100°C for 0.5 hour. Fig 2.5 shows a schematic representation of the procedure.



\*50°C/1 hr, 60°C/1hr, 70°C/1hr, 100°C/0.5

**Fig 2.5: Schematic representation of epoxy-amine neat network.**



**Fig 2.6: A general equation showing synthesis of TN-neat**

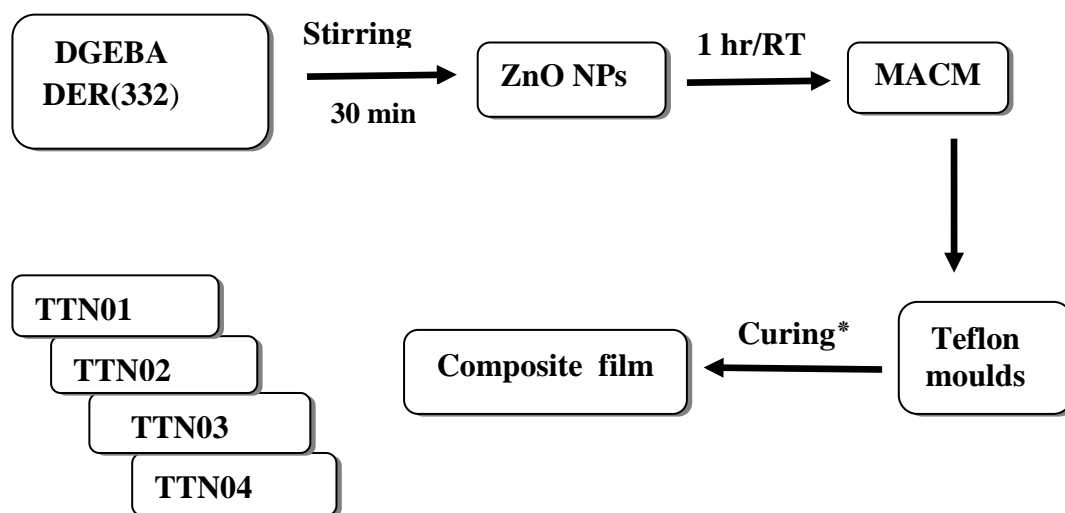
### 2.3.2.2 SYNTHESIS OF EPOXY-ZINC OXIDE NANOCOMPOSITES

These systems will be abbreviated as TTN. In order to synthesize epoxy-amine-ZnO nanocomposites, different sizes of calcined or uncalcined ZnO nanoparticles with different percentages were used. Percentage of ZnO nanoparticles in these series varied from 0.5% to 2.0%.



### 2.3.2.2.1 Procedure

For this purpose calculated amount of DGEBA was taken in a 30mL beaker. It was vigorously stirred and allowed to melt for half an hour at room temperature. Then ZnO was added and mixture was stirred vigorously for 1 hour. During this period the mixture was degassed for 10 minutes, in a vacuum oven to remove air bubbles and sonicated to ensure uniform distribution of particles in the composite film. Finally MACM was added and stirred for 20 minutes. Both the epoxy and diamine were taken in stoichiometric ratios i-e (NH/E=1). Controlled thickness was achieved by casting the measured amount of reaction mixture in the preheated moulds and then placing the moulds on a plane surface in the oven at 50°C for 1 hour, 60°C for 1 hour, 70°C for 1 hour, 80°C for 1 hour, 90°C for 1 hour and 100°C for 6-8 hours. Fig 2.7 shows the schematic representation of procedure adopted for preparation of epoxy-MACM-ZnO nanocomposites.



\*50°C/1 hr, 60°C/1 hr, 70°C/1 hr, 80°C/1 hr, 90 °C/1 hr, 100°C/6-8 hrs

**Fig 2.7: Schematic representation of epoxy-amine-ZnO nanocomposites**

The composition of all series in the system of DGEBA and MACM are given in tables 2.2-2.5.

#### 2.3.2.2.2 Series 1: (TTN 01)

In series 1, the surface functionalized uncalcined ZnO nanoparticles which were obtained after 15 min of reflux were used. The size of particles estimated from Scherrer equation <sup>[111]</sup> was 35.62 nm. The compositions synthesized in this series are given in Table 2.2

**Table 2.2 Composition Wt% of TTN 01**

<b>S.No.</b>	<b>DGEBA Wt%</b>	<b>MACM Wt%</b>	<b>ZnO Wt%</b>	<b>Sample Code</b>
1	74.12	25.37	0.5	TTN01-1
2	73.77	25.23	1	TTN01-2
3	73.39	25.11	1.5	TTN01-3
4	73.01	24.99	2	TTN01-4

**2.3.2.2.3 Series 2: (TTN02)**

In series 02, calcined ZnO nanoparticles obtained after 15 min of reflux were used. After calcination size of particles estimated from Scherrer equation was 37nm. The compositions synthesized in this series are given in Table 2.3.

**Table 2.3 Composition Wt% of TTN 02**

<b>S.No.</b>	<b>DGEBA Wt%</b>	<b>MACM Wt%</b>	<b>ZnO Wt%</b>	<b>Sample Code</b>
1	74.12	25.37	0.5	TTN02-1
2	73.77	25.23	1	TTN02-2
3	73.39	25.11	1.5	TTN02-3
4	73.01	24.99	2	TTN02-4

**2.3.2.2.4 Series 03: (TTN03)**

In series 03, surface functionalized uncalcined ZnO nanoparticles obtained after 30 min of reflux was used. The size of particles estimated from Scherrer equation was 42nm. The compositions synthesized in this series are given in Table 2.4.

**Table 2.4 Composition Wt% of TTN 03**

<b>S.No.</b>	<b>DGEBA Wt%</b>	<b>MACM Wt%</b>	<b>ZnO Wt%</b>	<b>Sample Code</b>
1	74.13	25.37	0.5	TTN03-1
2	73.77	25.23	1	TTN03-2
3	73.39	25.11	1.5	TTN03-3
4	73.01	24.99	2	TTN03-4

**2.3.2.2.5 Series 04: (TTN 04)**

In series 04, calcined ZnO nanoparticles obtained after 30 min of reflux was used. After calcination size of particles estimated from Scherrer equation was 44nm. The compositions synthesized in this series are given in Table 2.5.

**Table 2.5 Wt% Composition of Series 04**

<b>S.No.</b>	<b>DGEBA Wt%</b>	<b>MACM Wt%</b>	<b>ZnO Wt%</b>	<b>Sample Code</b>
1	74.12	25.37	0.5	TTN04-1
2	73.77	25.23	1	TTN04-2
3	73.39	25.11	1.5	TTN04-3
4	73.01	24.99	2	TTN04-4

## **RESULTS AND DISCUSSION**

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This chapter is divided into two parts, one consisting of analysis of particle while the other part describes the analysis of composite films. Epoxy zinc oxide nanocomposites contain epoxy (DGEBA) and MACM as matrix. Nanoparticles were analyzed by ultra violet spectroscopy (UV), Fourier transform infrared spectroscopy (FTIR), X ray diffraction (XRD), thermogravimetric analysis (TGA), Photoluminescence (PL), and scanning electron microscopy (SEM). The nanocomposites were analyzed by FTIR, XRD, Differential scanning calorimetry (DSC), Scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and Dynamic mechanical thermal analysis (DMTA).

### **3.1 PARTICLES ANALYSIS**

The as-synthesized ZnO NPs were characterized through following techniques:

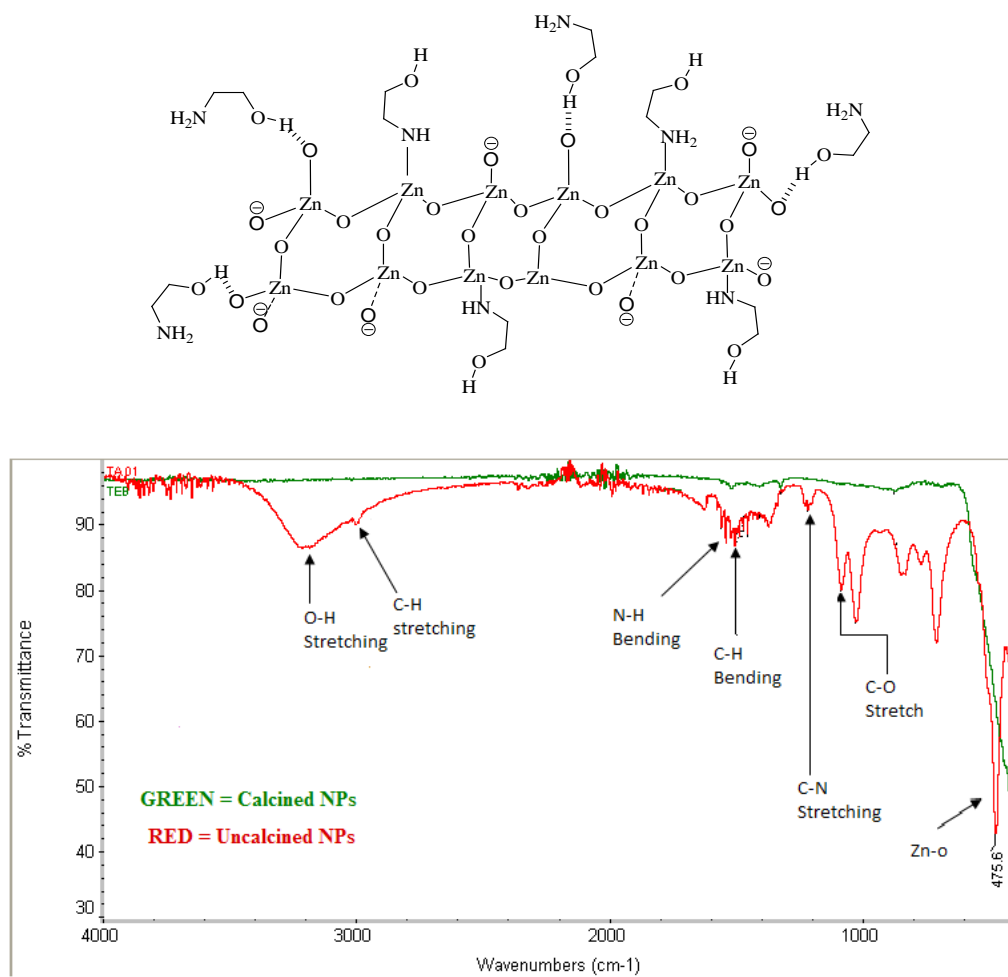
#### **3.1.1 PHYSICAL APPEARANCE**

The particles synthesized were white and powdered.

#### **3.1.2 FT-IR SPECTROSCOPY**

IR of particles was carried out so as to know about the functional groups present at the surface of the particles. The un-calcined ZnO nanoparticles were dried at 100°C so that the capping agent/surfactant was still present on the surface of the particles. 2-Amino ethanol was used as capping agent functionalized with ZnO nanoparticles. There are two main advantages of 2-aminoethanol in the synthesis of ZnO. Initially it controls the particle size by limiting the growth of the particles after the nucleation. Secondly it provides a side group on surface of ZnO nanoparticles which help in further conjugation with polymer matrix. 2-aminoethanol eliminates the surface defects which would affect the optical properties of the ZnO nanocrystals <sup>[112]</sup>. Figure 3.1 shows a typical FTIR spectrum of a representative ZnO prepared in 2-aminoethanol. 2-aminoethanol contains two important groups i.e., NH<sub>2</sub> and OH, which would like to be linked with surface of ZnO crystal. As nitrogen atom of amino group contains a pair of electron and acts as a nucleophile. The nucleophilicity of nitrogen atom is greater than oxygen, so it might be expected that nitrogen atom

linked with zinc hydrogen atom of the hydroxyl group might forms hydrogen bonding with oxygen of ZnO.



**Figure 3.1: IR spectra of calcined and un-calcined ZnO NPs**

FTIR spectrum of ZnO nanoparticles was acquired at 400-4000  $\text{cm}^{-1}$ . The broad band at  $3284 \text{ cm}^{-1}$  indicated the  $-\text{OH}$  stretching mode of hydroxyl groups. The peak of  $-\text{NH}_2$  group overlapped with the broad signal of  $-\text{OH}$  group, so its presence was confirmed by the peak at  $1557 \text{ cm}^{-1}$  due to bending mode of vibration of N-H group. Another absorption band at  $2930 \text{ cm}^{-1}$  is due to the C-H stretching frequency of  $-\text{CH}_2$  of 2-aminoethanol along with the peak at  $1456 \text{ cm}^{-1}$  that corresponds to the C-H bending of  $-\text{CH}_2$  group. The band at  $1048 \text{ cm}^{-1}$  corresponds to stretching vibration of C-O of alcoholic group. A strong and intense peak at  $475 \text{ cm}^{-1}$  represented the Zn-O stretching vibrations <sup>[91]</sup>.

**Table 3.1: IR frequencies of surface functionalized ZnO NPs**

2-Aminoethanol	Structural unit	Frequency $\text{cm}^{-1}$	Stretching/Bending Vibrations
$  \begin{array}{c}  \text{O}-\text{H} \\    \\  \text{CH}_2 \\    \\  \text{CH}_2 \\    \\  \text{H}-\text{N}-\text{H}  \end{array}  $	O-H	3284	Stretching
	C-H	2930	Stretching
	C-H	1456	Bending
	N-H	1557	Bending
	C-N	1216	Stretching
	C-O	1084	Stretching
	<b>Zinc oxide</b> Zn-O	Zn-O	475

In the same figure 3.1, the FTIR of calcined nanoparticles is shown. ZnO nanoparticles were calcined at  $600^\circ\text{C}$  in open air furnace. The calcination of nanoparticles was carried out for 3 hours. At this high temperature all the organic content was burnt off and pure zinc oxide network was left. This was confirmed by the absence of any organic moiety in IR spectrum of calcined particles. Only the peak of Zn-O was observed at  $450\text{ cm}^{-1}$ .

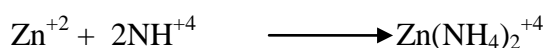
On the basis of previous studies, the mechanism proposed for the synthesis of ZnO nanoparticles was as follows.

At the first step, a primary solution was obtained by adding ammonia in water. In this way ammonia solution exists in the form of  $\text{NH}_4^+$  and  $\text{OH}^-$  ion.



Zinc nitrate hexahydrate is dissolved in the solution to forms  $\text{Zn}^{+2}$  ions and  $\text{NO}_3^-$  ions.

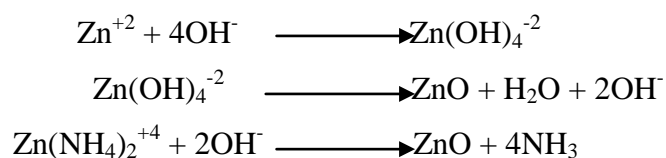
In the second step  $\text{NH}_4\text{OH}$  solution is added to the solution of  $\text{Zn}^{+2}$  ions.  $\text{Zn}^{+2}$  interacts with  $\text{NH}_4^+$  ions to form zinc ammonium complex due to Van der Waals forces [89].



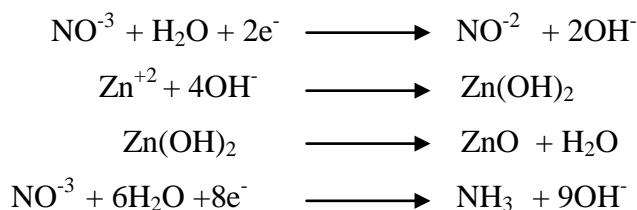
Ammonium ion adjust the pH of reaction mixture and control the formation of  $\text{Zn}(\text{OH})_4^{2-}$ . Zinc cations occur largely in four coordination as tetrahedral complexes.

In this work the two complexes,  $\text{Zn}(\text{NH}_4)_2^{+4}$  and  $\text{Zn}(\text{OH})_4^{-2}$ , were generated in the solution and became the precursor of ZnO.

It was reported previously that ratio of  $\text{Zn}(\text{OH})_4^{-2}$  to the  $\text{Zn}(\text{NH}_4)_2^{+4}$  determine the morphology of ZnO crystals. The stability of  $\text{Zn}(\text{NH}_4)_2^{+4}$  complex at pH=11 are higher than the  $\text{Zn}(\text{OH})_4^{-2}$  complexes. Hence, the  $\text{Zn}(\text{NH}_4)_2^{+4}$  ions could serve as the complex agent triggering the formation of ZnO nuclei.

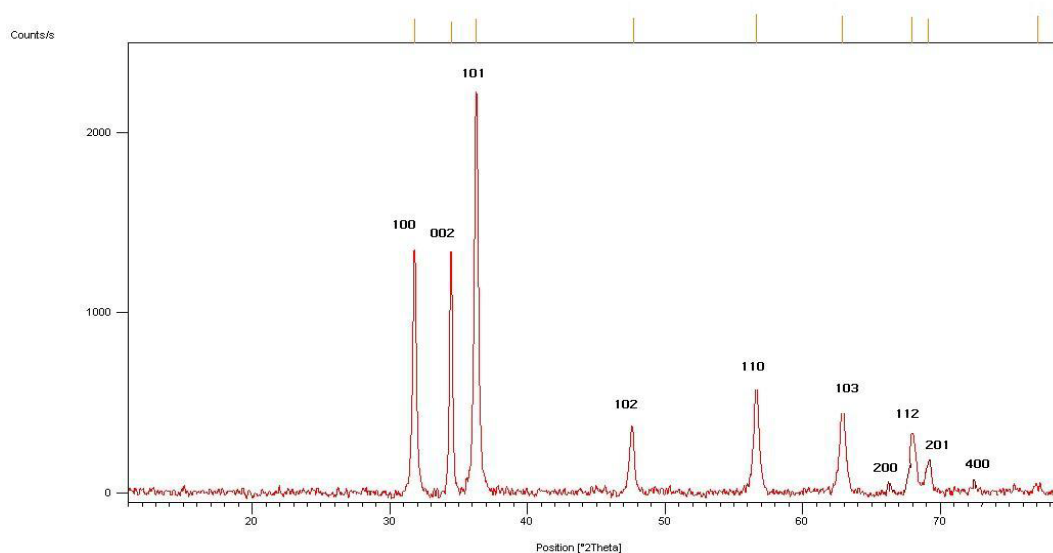


The reduction of nitrate ion  $\text{NO}^{-3}$  to  $\text{NO}^{-2}$  and even the  $\text{NH}_3$  also contributed to the growth of ZnO [91, 113].



### 3.1.3 X-RAY DIFFRACTION ANALYSIS

The crystallinity, phase characteristics and purity of the ZnO-NPs were determined by using XRD spectra of the samples.



**Figure 3.2: XRD of ZnO nanoparticles**

All the reflections were indexed as pure hexagonal wurtzite ZnO phase. XRD peaks indicated that the products were pure powders with no observable peak relevant to impurities such as Zn(OH). The sharp peaks indicated that ZnO were well

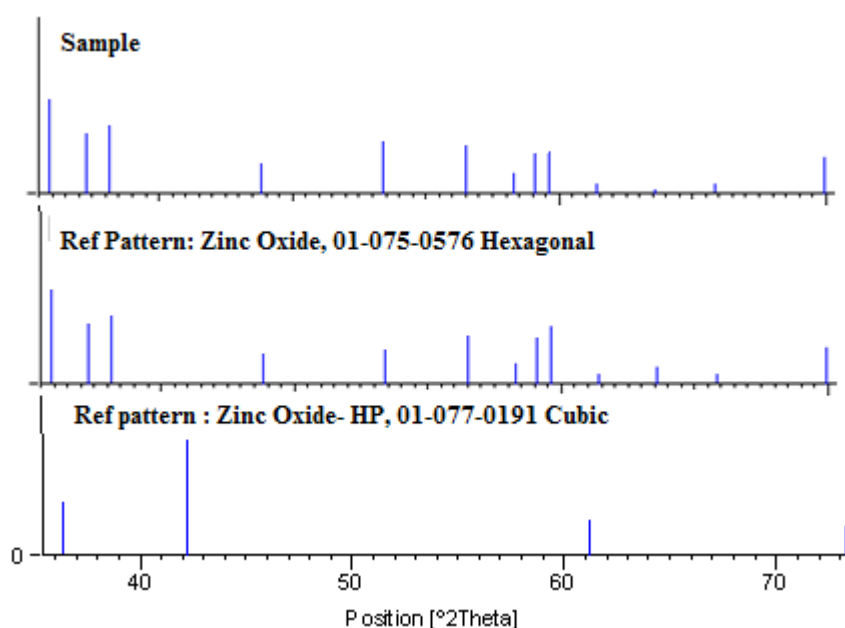
crystallized. In order to determine the average crystallite size of the nanoparticles. The Scherrer formula can be used which is given by equation I.

$$d = K\lambda/B\cos\theta \dots\dots\dots (Eq I)$$

Where  $d$  is the mean crystallite size of the powder,  $\lambda$  is the wavelength of Cu  $K\alpha$  radiation, ( $\lambda=1.5405\text{\AA}$ ),  $B$  is the full width at half maximum (FWHM) intensity of the peak in radian,  $\theta$  is the Bragg's diffraction angle and  $K$  is the constant usually equal to  $\sim 0.9$  [91]. The crystallite size of the nanoparticles was found to range from 9 nm to 70 nm.

Furthermore XRD spectrum clearly showed that the intensity ratio of the peaks belonging to the phase (100) and (101) and that between (002) and (101) planes are relatively higher compared to that of the bulk ZnO. These results clearly indicated the preferential growth of ZnO nanoparticles along some particular lattice direction during monostructure formation [114].

Figure 3.3 shows XRD peak correlation of ZnO with the reference. The reference number 01-075-0576 corresponds to the peak pattern of hexagonal structure while the reference number 01-077-0191 corresponds to the peak pattern of cubic structure. The  $2\theta$  values of sample ZnO coincide with those of the standard hexagonal ZnO structures. It is in agreement with the standard hexagonal wurtzite crystal structures with space group  $P63mc$ . Furthermore, there was no distinct peaks observed which indicate the high purity of the nanocrystals [114].



**Figure 3.3 XRD peak correlation of ZnO with the reference**

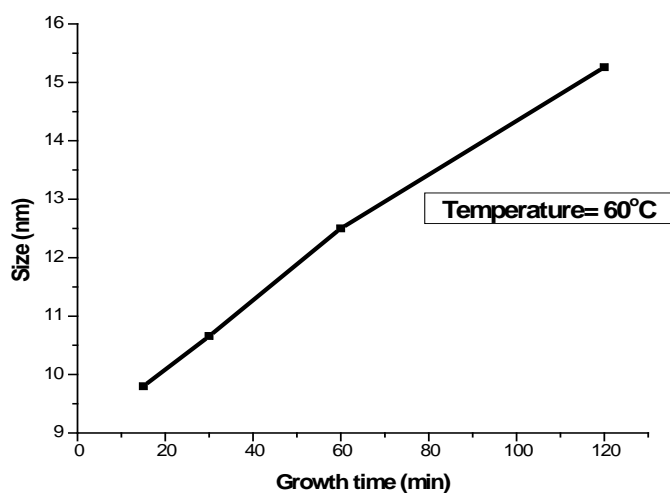


The size of ZnO NPs was varied by changing time and temperature of the reaction mixture. Two parameters were studied:

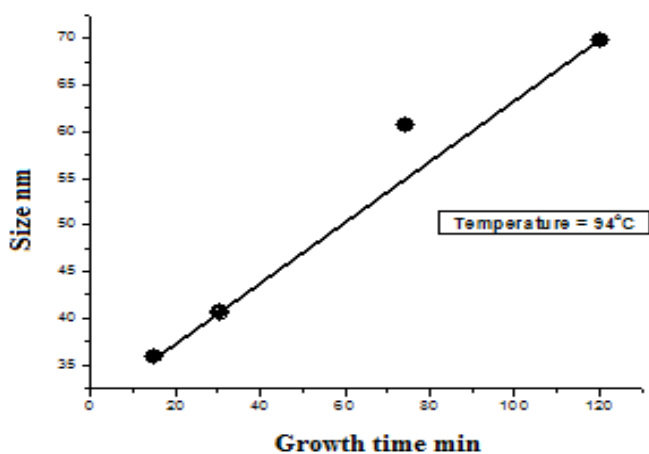
- Effect of growth time on size of nanoparticles size and
- Effect of temperature on nanoparticles size.

**a) Effect of growth time on nanoparticles**

To study the effect of growth on nanoparticles size, the reaction was carried out at constant temperature and different growth times were given to the particles. Figure 3.4 shows the relationship between growth time and size of particles at 60°C (a) and 94°C (b) respectively.



a)



b)

**Figure 3.4: Size of nanoparticles versus growth time a) 60°C b) 94°C**

XRD was used to identify the size of ZnO nanoparticles. Table 3.2 and 3.3 also indicates the linear relationship between growth time and size of nanoparticles.

**Table 3.2: Relationship between growth time & nanoparticles at 60°C**

S. No.	Growth time min	Size of particles nm
1	15	9.80
2	30	10.66
3	60	12.50
4	120	15.26

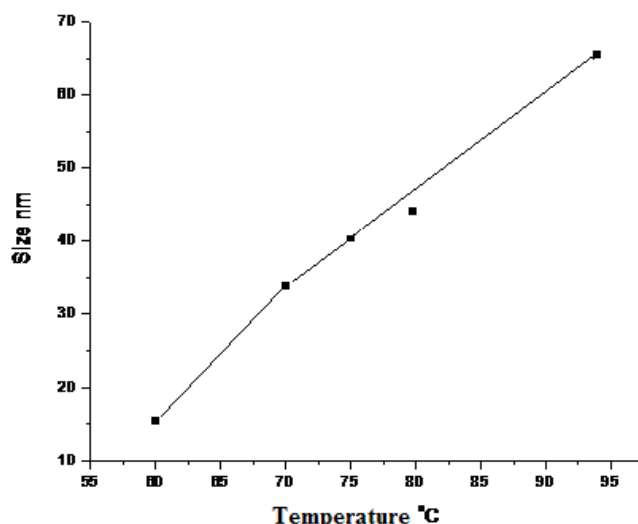
**Table 3.3: Relationship between growth time & nanoparticles at 90°C**

S. No.	Growth time min	Size of particles nm
1	15	35.62
2	30	40.28
3	60	65.40
4	120	69.50

As more time is given to the reaction mixture, initially synthesized small size ZnO particles aggregated to form large size particles. Growth time increases the crystal size of ZnO. Above tables also indicated that the particles obtained at 60°C were smaller in size than the particles obtained at 94°C.

**b) Effect of temperature on nanoparticles size**

In order to study the effect of temperature on nanoparticles, the reaction was carried out at different temperatures i.e., 60°C, 70°C, 75°C, 80°C and 94°C. A graph was plotted between temperature and size of nanoparticles as shown in figure 3.5.



**Figure 3.5: Size of nanoparticles versus reaction temperature**

From the above graph a straight line was obtained, showing again a linear relationship between the temperature and size of nanoparticles.

**Table 3.4 Relationship between temperature & nanoparticles size**

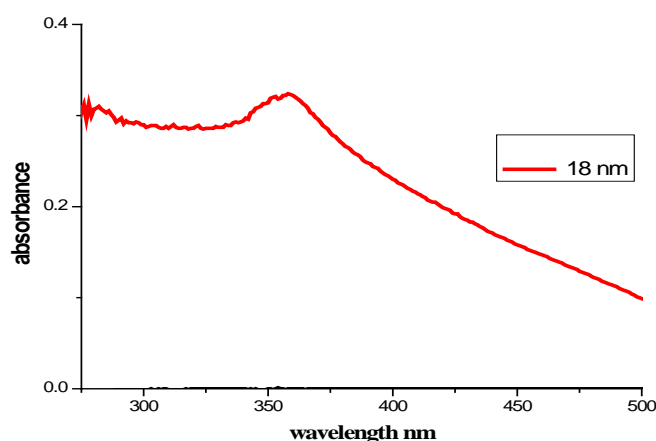
S. No	Temperature °C	Size of particles nm
1	60	15.26
2	70	33.82
3	75	40.28
4	80	43.15
5	94	65.40

Table 3.4 shows relationship between size of ZnO nanoparticles and temperatures which clearly indicates that small sized particles were obtained at low temperature. Moreover, with increase in temperature the particle size also increases [116]. At high temperature nanoparticles have high kinetic energy and have greater potential of combining together to form agglomerates.

### 3.1.5 ULTRA VIOLET SPECTROSCOPY

The UV-vis absorption spectrum of ZnO nanoparticles is shown in Figure 3.6. The UV-vis absorption spectrum of ethanolic nanoparticles solution was prepared by sonication of the particles in ethanol. ZnO is a semiconductor with band gap of 3.3 eV and shows maximum absorption at 380 nm. The absorption spectrum of 18 nm ZnO

nanoparticles showed a well defined exciton band at 358 nm showing a significant blue shift of 22 nm as compared to the bulk ZnO material [114]. The strong UV emission of ZnO nanoparticles should correspond to the excitation of electron from valance band to the conduction band as a result of the quantum confinement effect. The excellent UV emission property at room temperature may be attributed to the high purity and perfect crystallinity of the synthesized ZnO nanoparticles [90]. Nanometric material has proven to be excellent for UV absorption and can be used in sunscreen lotions.



**Figure 3.6: UV-vis spectrum of ZnO nanoparticles**

The band gap of these 18 nm sized zinc oxide nanoparticles can be calculated by using the value of  $\lambda_{\text{max}}$  obtained from UV analysis, following equation II:

$$E = hc/\lambda \dots \dots \dots \text{(EqII)}$$

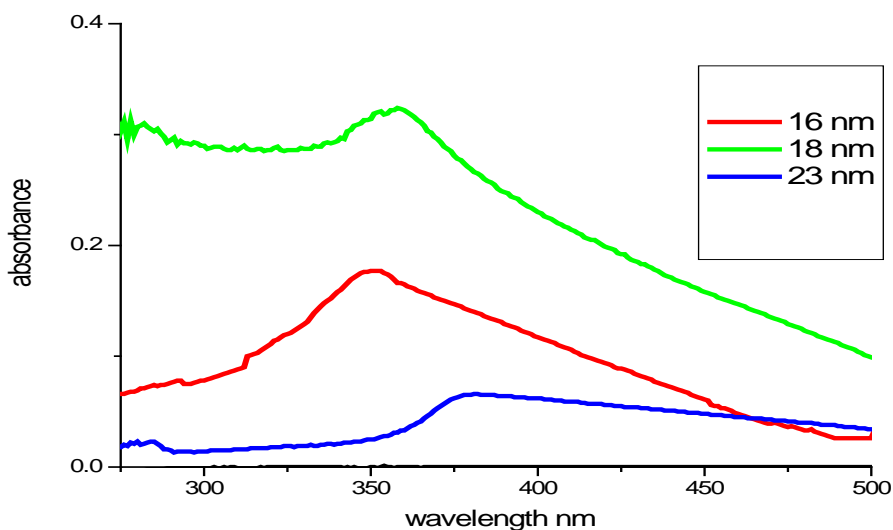
Where, h= Planks constant, its value is  $6.625 \times 10^{-34} \text{ s}^{-1}$ , c is the velocity of light, which is  $3 \times 10^8 \text{ m/s}$ , and  $\lambda$  is the wave length at which maximum absorption takes place. By putting all these values in above equation a value of 3.46 eV is obtained.

$$\begin{aligned} E &= 5.5 \times 10^{-19} \text{ J} \\ &= 3.46 \text{ eV} \end{aligned}$$

Bulk ZnO has a band gap of 3.26 eV, where as the band gap of 18 nm ZnO NPs is 3.46 eV. So, band gap increases as the particle size decreases.

Three differently sized ZnO nanoparticles i.e., 16, 18 & 23 nm were taken and their UV spectra were recorded, to check the relationship between particle size and maximum absorption, as shown in figure 3.7. It was clearly shown from UV spectrum that ZnO nanoparticles of 16, 18 & 23 nm showed maximum absorption at 352 nm, 358 nm & 375 nm, respectively. It was revealed from UV spectra that as the particle

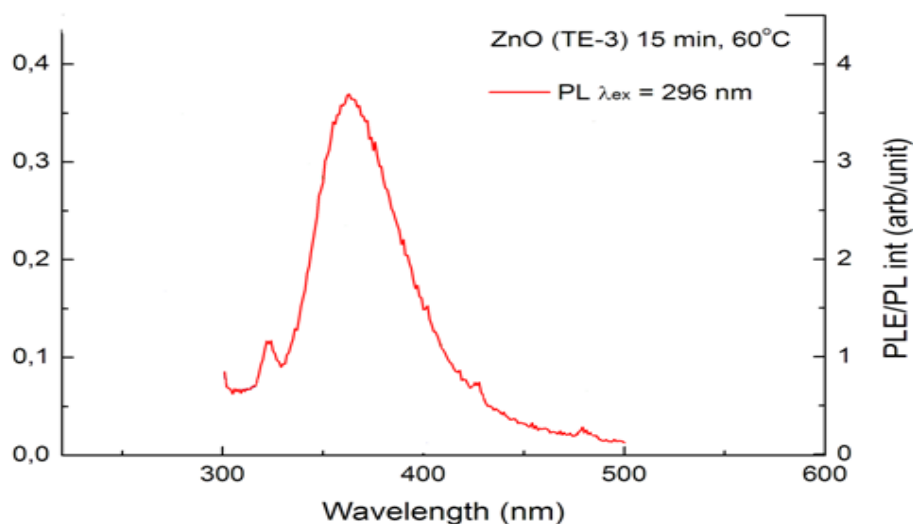
size decreases the value of  $\lambda_{\max}$  also decreased. The band gaps of these particles were 3.52 eV, 3.46 eV & 3.31 eV. With the decrease in particle size, the energy gap between valence band and conduction band increases and more amount of energy is required for transitions. Thus smaller size particles absorbed more energy and showed  $\lambda_{\max}$  at comparatively shorter wavelength as compared to larger size particle



**Figure 3.7: Comparative UV spectra of ZnO nanoparticles**

### 3.1.6 PHOTOLUMINESCENCE SPECTROSCOPY

In ZnO nanoparticles, the luminescence behavior is of particular interest from both physical and applied aspects. Photoluminescence (PL) of the ZnO nanoparticles was measured at 60°C as shown in figure 3.8. A sharp near band edge emission at 375 nm, a weak emitted band of blue emission at 420 nm, and a green band at 460-500 nm can be observed. The near band-edge emission is attributed to the well-known recombination of free excitations. The weak green band emission corresponds to singly ionized oxygen vacancies in ZnO resulted from recombination of a photogenerated hole with the single ionized charge state of the defect. The weak green emission also implies that there are few surface defects in the ZnO nanoparticles<sup>[117]</sup>.

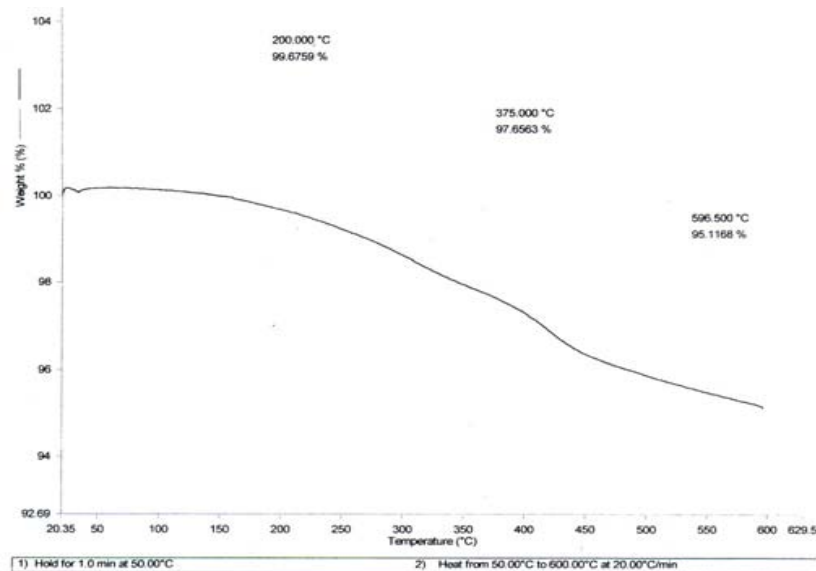


**Figure 3.8: Photoluminescence spectrum of ZnO nanoparticles**

### 3.1.7 THERMOGRAVIMETRIC ANALYSIS

Thermal analytical technique, such as TGA was used to determine the presence of impurities along the possible energy exchange reaction during the dissociation or decomposition process. Impurities and other species either escape or decompose into other volatile products, leaving the nanoparticles in their purest form.

TGA thermogram of surface functionalized ZnO nanoparticles is displayed in figure 3.9. The weight loss took place in three stages, the first stage occurred in the range of 40-200°C, and is related to the removal of physically absorbed water from the nanoparticles. This is about 0.32% of nanoparticles, indicating the presence of water retained during washings. The second stage of weight loss occurred in the range of 225-375°C. It is about 2.01% and is attributed to water formed from condensation of hydroxyl groups on a particle's surface i.e., in the form of  $Zn(OH)_2$ . The third weight loss took place in the range of 400-500°C. This weight loss is about 2.54% and is caused by the condensation of zinc oxide groups or/and thermal decomposition of 2-aminoethanol [77].

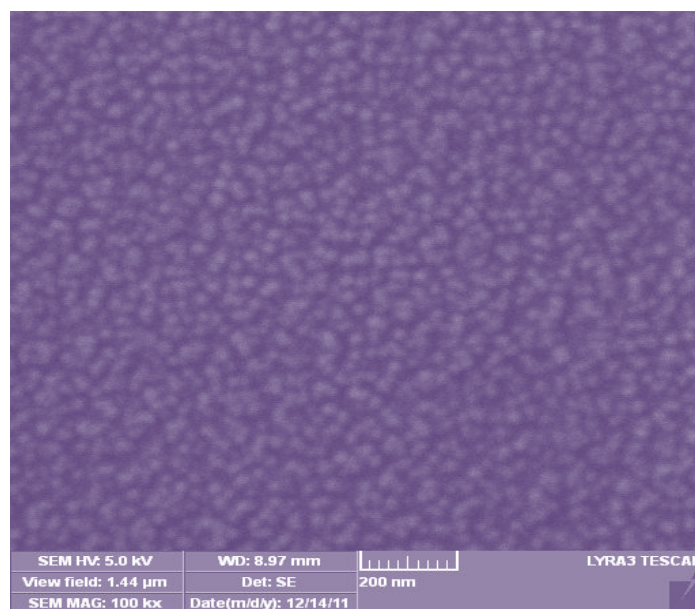


**Figure 3.9: TGA of ZnO nanoparticles**

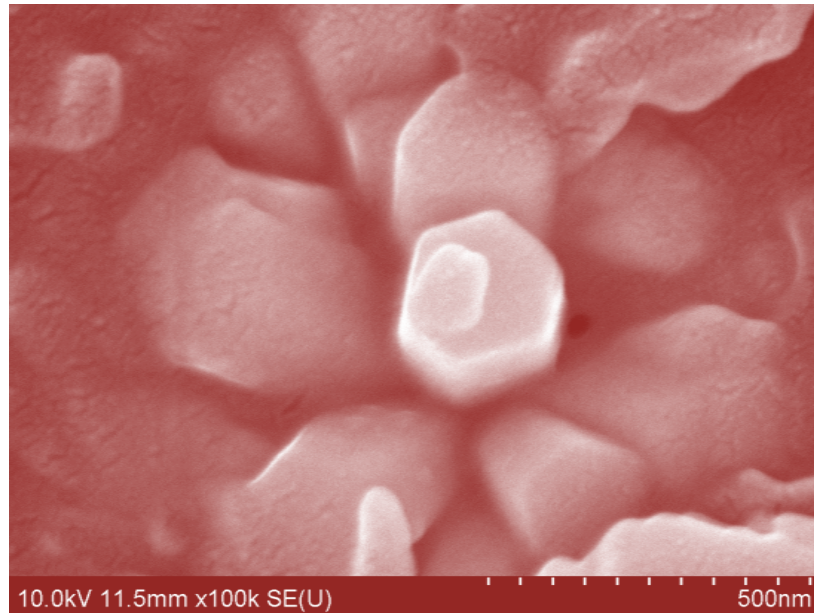
### 3.1.8 SCANNING ELECTRON MICROSCOPY

The SEM micrograph of sample gives information about morphology, particles distribution and particles size. Figure 3.10 (a) shows the SEM image of surface functionalized ZnO nanoparticles obtained at pH =11.2. The low magnification view demonstrates that ZnO nanoparticles have uniform size distribution, non-agglomerated, and or bead like.

At high magnification power, regular, well dispersive narcis-like architecture was observed. Individual narcis-like nanostructures composed of central core with six petals around it.



**Figure 3.10 (a): SEM image of ZnO nanoparticles( Resolution 200 nm)**



**Figure 3.10 (b): SEM image of ZnO nanoparticles (Resolution 500 nm)**

### **3.2 CHARACTERIZATION OF ZnO NANOCOMPOSITE SYSTEMS**

ZnO nanoparticles are the promising material for being used in epoxy amine composites. The key point of ZnO nanoparticles is the size uniformity, surface passivation and chemical stability, wear resistant, heat resistance, corrosion resistance which remains to be a major interest. For this reason, many studies were dealing with the stabilization of composite by using ZnO nanoparticles in polymeric networks. There are two important advantages for ZnO-polymeric nanocomposites. One is that the polymeric matrix can make nanometer scale; ZnO nanoparticles homogeneously dispersed in the composites and improve the stability, dispersion and mechanical strength of the materials. Second is that the surface of the ZnO nanoparticles could be modified by the polymeric matrix *via* the interactions between the two components [104].

In these series, MACM is used as a diamine and ZnO as inorganic filler. The TN-neat was used as reference for the TTN composite systems. Initially two differently sized ZnO nanoparticles were selected for the synthesis of nanocomposites. Selected ZnO nanoparticles were further calcined and used for the synthesis of two series of nanocomposites. In all series the percentage of ZnO varied from 0.5% to 2%. The ZnO nanoparticles were blended with stoichiometric amounts of DGEBA and MACM while ensuring the formation of homogenous mixture. The



mixture was then poured into the uniform sized moulds for shaping into thin strips for thermo-mechanical analysis.

### 3.2.1 FT-IR SPECTROSCOPY

FTIR spectrum of epoxy-amine neat network is shown in figure 3.11. Curing of MACM with DGEBA at 100°C produces three dimensional network. The characteristic peaks in IR spectrum of MACM are those of -NH<sub>2</sub> functional group at 3380 cm<sup>-1</sup> and 3270 cm<sup>-1</sup> correspond to the symmetric and asymmetric vibrations of primary N-H bond. The NH<sub>2</sub> functionality of amine opens the epoxy ring of DGEBA, to give tertiary amine C-N, showing a strong transmittance peak at 1230 cm<sup>-1</sup> with the disappearance of absorption bands at 3300-3400 cm<sup>-1</sup>. The broad band at 3363 cm<sup>-1</sup> corresponded to the -OH stretching mode of hydroxyl groups which confirms the opening of oxirane ring. C<sub>sp</sub><sup>3</sup>-H stretching vibrations appeared in the region of 2918 and 2850 cm<sup>-1</sup>. Aromatic C=C appeared at 1606 cm<sup>-1</sup> while C<sub>sp</sub><sup>3</sup>-H bending vibrations due to CH<sub>3</sub> and CH<sub>2</sub> appeared in the region of 1455 and 1361 cm<sup>-1</sup>. A strong peak observed in the region of 1180 cm<sup>-1</sup> corresponds to Φ-O Stretching vibration. While the peak of alcoholic C-O appears at 1031 cm<sup>-1</sup> [118].

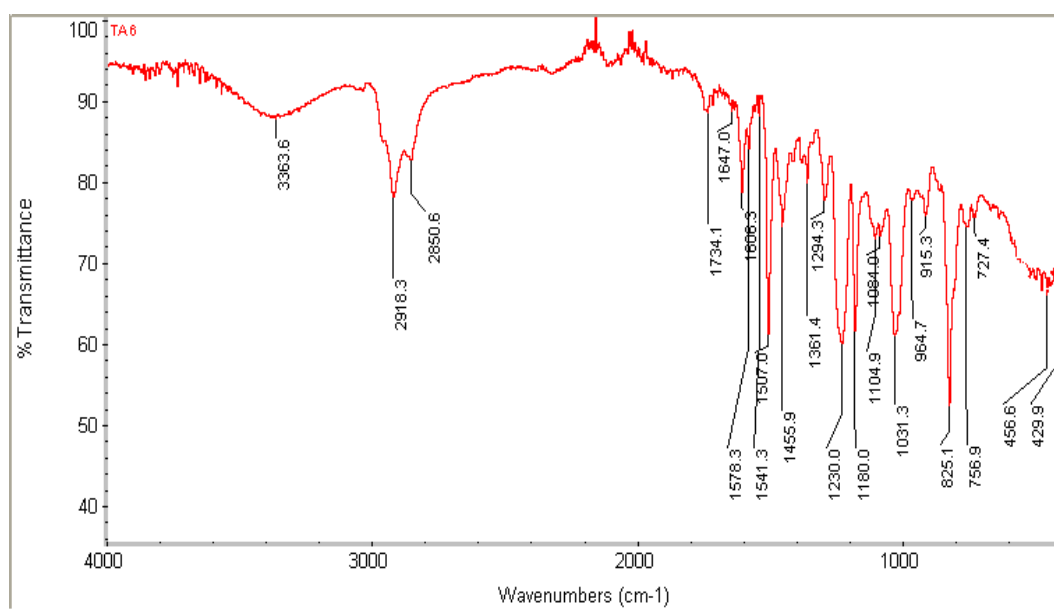


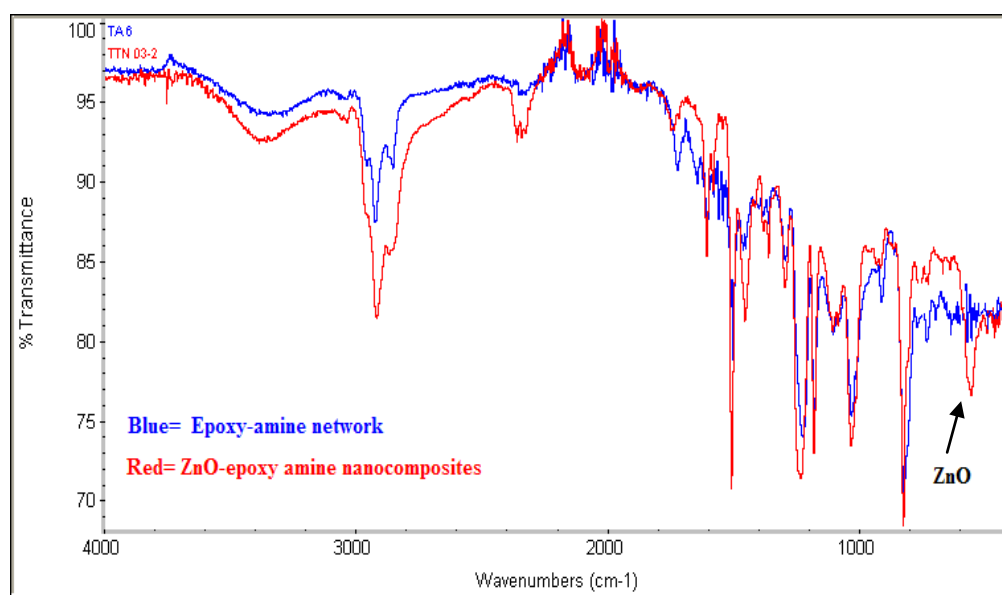
Figure 3.11: FTIR spectrum of epoxy-amine network

**Table 3.5 IR frequencies of epoxy-amine neat**

S. No.	Structural unit	Frequency $\text{cm}^{-1}$	Stretching/Bending Vibrations
1	O-H	3363	Stretching
2	C-H	2918, 2850	Stretching
3	C=C	1606	Stretching
4	C-H	1455, 1361	Bending
5	C-N	1230	Stretching
6	$\Phi$ -O	1180	Stretching
7	C-O	1031	Stretching

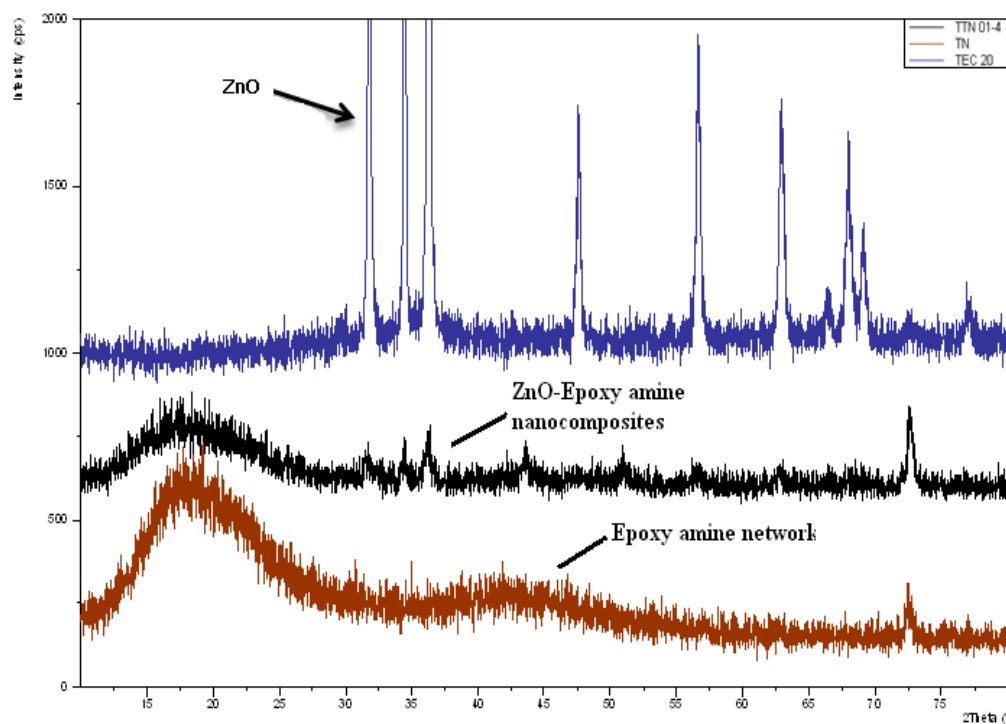
To study the effect of incorporation of ZnO nanoparticles in epoxy-amine matrix, FT-IR spectroscopy was performed. For better understanding the spectrum of epoxy-amine neat was compared with epoxy-amine ZnO nanocomposites. Figure 3.12 shows the combined FT-IR spectra of epoxy-amine matrix and ZnO epoxy-amine nanocomposites in the frequency range of 4000-400  $\text{cm}^{-1}$ . All peaks in both spectra are same. This shows that the curing of epoxy resin by amine is not interrupted by the introduction of ZnO nanoparticles the only difference is the presence of Zn-O stretching mode of vibration, which appears in the region of 550-475  $\text{cm}^{-1}$ .

From the spectral analysis of epoxy-amine-neat and epoxy-amine ZnO nanocomposite it is thus concluded that the epoxy group reacts with amine group. MACM thus establishing a chemical link between matrix and reinforcement.

**Figure: 3.12: Combined FTIR spectra of epoxy amine network and zinc oxide epoxy amine nanocomposite.**

### 3.2.2 X-RAY DIFFRACTION ANALYSIS OF NANOCOMPOSITES

ZnO nanoparticles were previously confirmed by XRD analysis. When ZnO NPs are blended with a polymer matrix their presence in the composite can be confirmed by the appearance of peaks corresponding to ZnO in ZnO epoxy-amine nanocomposites as shown in figure 3.13 while in epoxy-amine matrix this peak was absent instead amorphous structure was obtained.

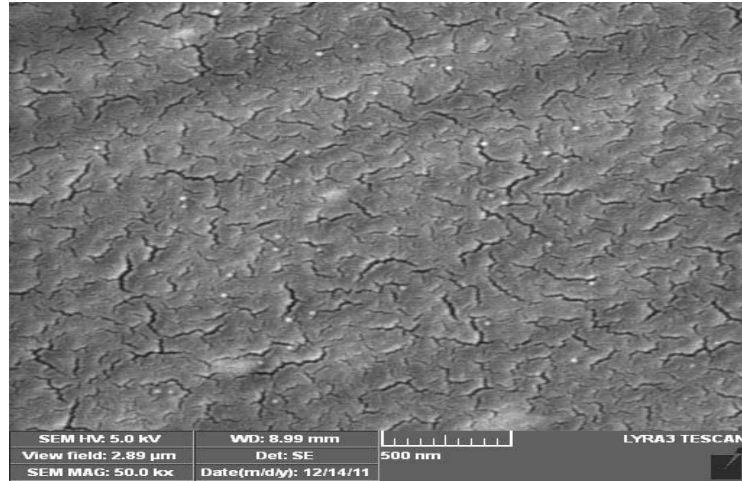


**Figure 3.13: XRD plots of ZnO, epoxy-amine neat network and ZnO epoxy-amine nanocomposites**

### 3.2.3 SCANNING ELECTRON MICROSCOPY OF NANOCOMPOSITES

SEM of nanocomposites film were done in order to see the influence of addition of zinc oxide nanoparticles on the type of interaction between the matrix, filler and the final size of the particles.

Figure 3.14 shows the SEM image of series # 04 with 2% ZnO NPs. It is clearly seen from SEM micrograph that the particles were homogeneously distributed in the matrix i.e., any region without filler was not visible. No agglomeration was observed which shows strong interaction between filler and matrix.



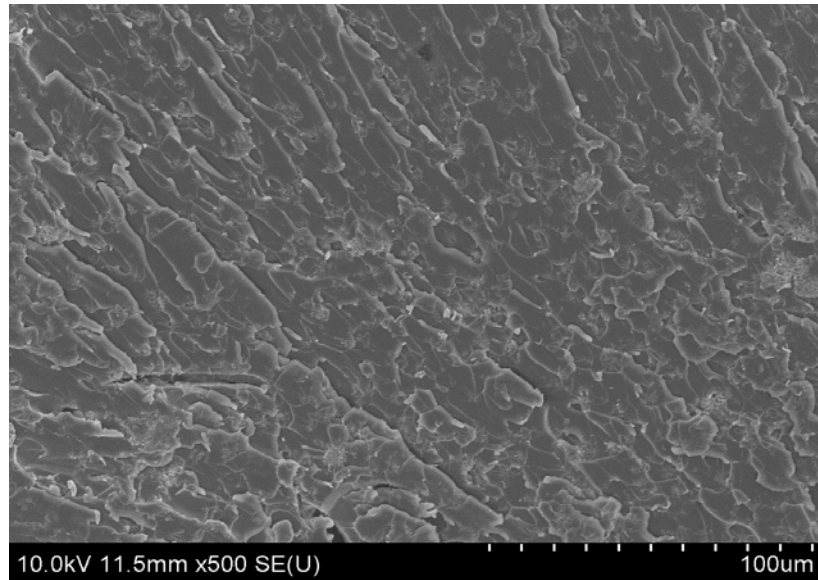
**Figure 3.14 (a) SEM image of epoxy-amine ZnO nanocomposites**

At high magnification power narciss-like ZnO nanoparticles were clearly observed in epoxy matrix. These ZnO nanoparticles were embedded in the polymer matrix.

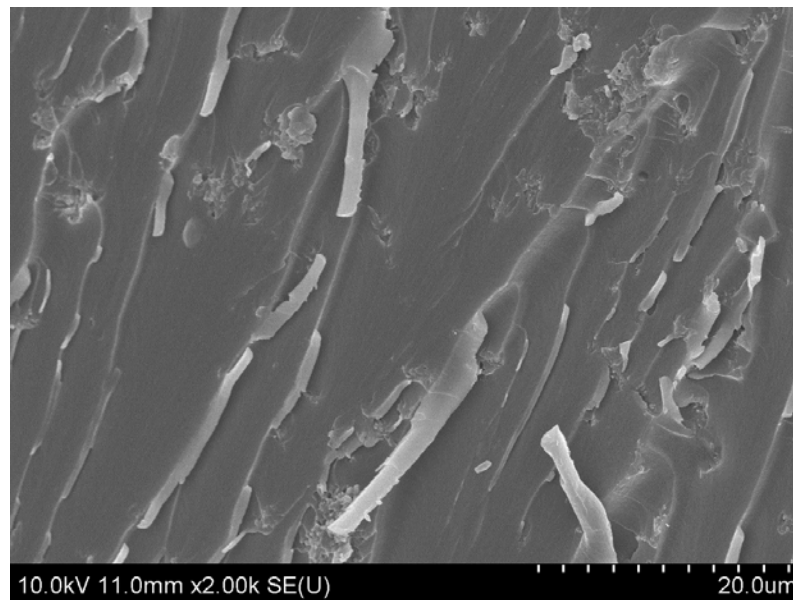
It is clearly seen from figure 3.15 (b) that nanoparticles significantly influence the surface morphology of the composites. Addition of nanoparticles can increase the surface roughness of matrix as shown in figure 3.14 (c) & (d).



**Figure 3.14 (b) SEM image of TTN 01-4, 2%ZnO NPs**



**Figure 3.14 (c) SEM image of TTN 02-4, 2%ZnO NPs**



**Figure 3.14 (d) SEM image of TTN 03-4, 2%ZnO NPs**

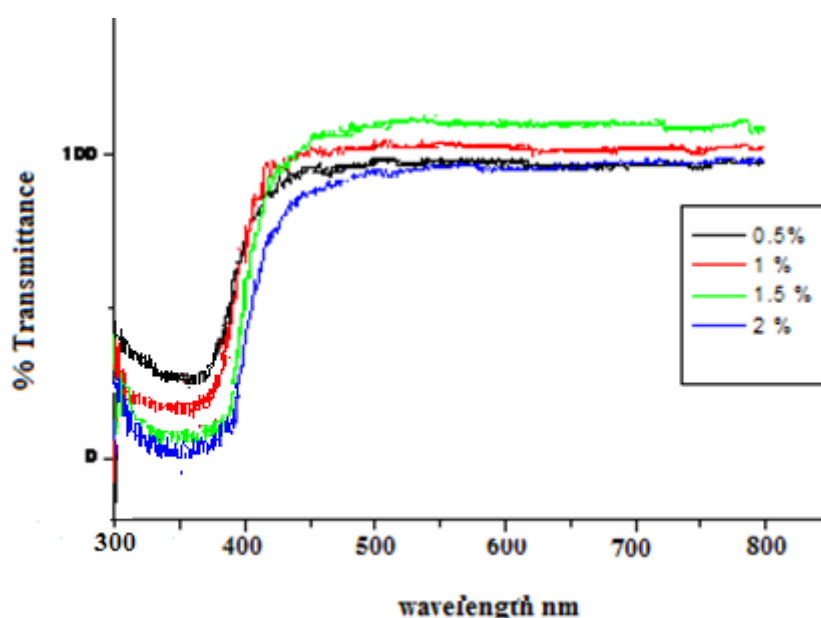
### **3.2.4 UV ANALYSIS OF NANOCOMPOSITES**

Zinc oxide is an inorganic material which absorbs ultra violet light. Zinc oxide is an extremely high UV- shielding material with low refractive index has been applied to the polymer as UV light filters. Through the incorporation of UV absorbents to the transparent epoxies can enhance significantly UV light resistance.

Transparent ZnO epoxy nanocomposites were prepared by the addition of ZnO nanoparticles into transparent epoxy resin and after that cured for a specific period of

time. The UV-vis transmittance spectra of ZnO epoxy nanocomposites, series # 3 (TTN03), are shown in figure 3.15.

In each series of nanocomposites, the percentage of ZnO nanoparticles was 0.5%, 1.0%, 1.5%, & 2.0%. As the percentage of ZnO in nanocomposites increases the % transmittance decreases and they shows more UV absorbance. These composite films showed UV transmittance above 450 nm. Below 450 nm these nanocomposite exhibit almost perfect UV light shielding efficiency. Hence ZnO nanoparticles increased the UV light shielding efficiency and high visible light transparency of epoxy amine matrix. Both these properties are preferred for transparent packing material<sup>[107]</sup>.



**Figure 3.15: UV-vis spectra of ZnO nanocomposites (TTN 01)**

### 3.2.5 THERMAL ANALYSIS

The diglycidyl ether of bisphenol-A (DGEBA) is the most commonly used epoxy resin as it has many attractive features such as fluidity, low shrinkage during cure and ease of processing. The cured products have good physical strength, stiffness, adhesion, excellent moisture, solvent and chemical resistance. Their main problem is relatively poor thermal stability and flame resistance which limits their applications in some demanding areas such as aerospace and electronic industry<sup>[35]</sup>.

So, the thermal properties of neat polymer can be modified by the addition of the reinforcement. Thermal behavior of the ZnO nanocomposites was studied to see the effect of the ZnO nanoparticles on  $T_g$  of epoxy matrix.

### 3.2.5.1 DIFFERENTIAL SCANNING CALORIMETRY OF EPOXY-AMINE NEAT

The objective of DSC studies was to determine the glass transition temperature and crosslinking density neat polymer matrix and change in these parameters after the addition of nanoparticles.

For the determination of glass transition measurements ( $T_g$ ) of epoxy-amine neat matrix, the temperature was raised with the rate of 10°C/min. First scan i.e., heating scan was obtained in the range of 0-350°C and the same sample was cooled between 350-0°C.

The glass transition of epoxy matrix was appeared at 91°C. Below this temperature polymeric chain were remains at their specific positions. At 91°C, the polymeric chains showed mobility and slide over one another.

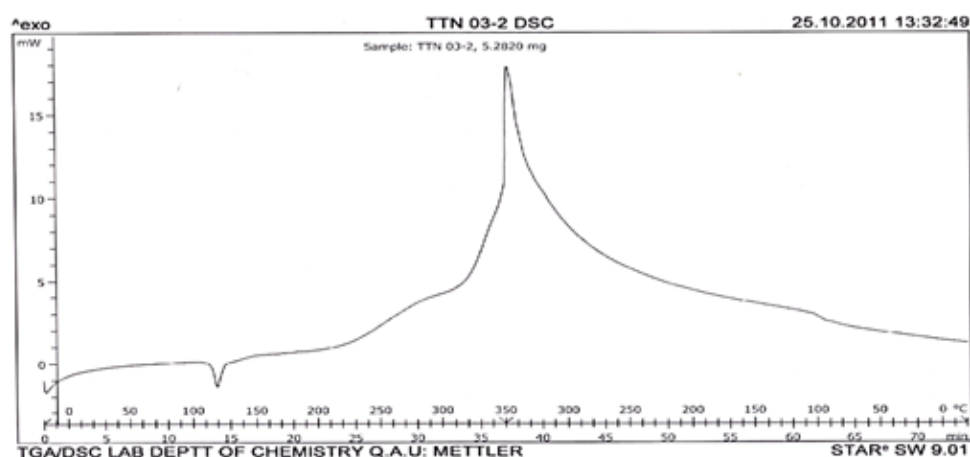
So far, DSC results of only 1 series i.e., TTN 03, have been obtained and are discussed below. Table 3.6 shows the  $T_g$  values obtained for the epoxy nanocomposites at different nano-ZnO concentrations.

**Table 3.6:  $T_g$  values for the epoxy nanocomposites at different nano-ZnO concentrations for TTN 03**

<b>% of ZnO NPs</b>	<b><math>T_g</math> values °C</b>	<b>Sample codes</b>
0	91	Neat
0.5	100	TTN03-1
1.0	100	TTN03-2
1.5	100	TTN03-3
2.0	99	TTN03-4

From table 3.6, it is clearly indicated that glass transition of nanocomposites with different concentration of ZnO nanoparticles is higher than epoxy amine neat network. There was significant increase in  $T_g$  from 91°C to 100°C by the addition of nanoparticles <sup>[119]</sup>. An increase in  $T_g$  was believed to be due to the formation of three dimensional polymeric network between the resin matrix and the inorganic nanoparticles which restricted the movements of

polymeric chains. The entropy and the chain kinetics were greatly altered within the interface region, and the polymer chain experience sufficient constrains. It was these constrain forces which in consequence shift  $T_g$  to higher temperature. Increase in glass transition temperature may lead to increase in cross-linking density of nanocomposites. The  $T_g$  values was slightly decreased for 2% ZnO loading, which may be explained in terms of increase in free-volume by increasing the % of ZnO nanoparticles, causing slightly loose packing of polymeric chain, which in consequence assisted the segmental motion of the polymer on smaller scale. Figure 3.15 shows the DSC thermogram of the TTN 03-2, having 1.0% of ZnO nanoparticles.



**Figure 3.15:  $T_g$  of TTN 03-2**



## CONCLUSION

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The recent work has provided much insight as to know about effect of ZnO nanoparticles on various properties of epoxy-amine network. At the end this work can be summarized by a few basic yet important conclusion

- Co-precipitation method was adopted to synthesize variable size of ZnO NPs by varying different parameters and 2-aminoethanol was used as capping agent.
- As-synthesized ZnO NPs were UV active and also showed photoluminescent property.
- 16 compositions were synthesized by using four differently sized ZnO NPs, and varying the percentage of ZnO NPs from 0.5% - 2.0%.
- SEM images show very well dispersion of NPs in composites film.
- These nanocomposite films have high UV shielding property, which transmit light in visible region and absorb UV light.
- Nanocomposites have high glass transition temperature as compared to neat epoxy-amine matrix.

## **FUTURE PLAN**

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Nanoparticles are a topic of growing interest now a day. A great deal of work has already been done on them, and scientists are looking forward to explore even easier pathways to achieve nanoparticles. Nanotechnology is a tool, used for the betterment of mankind, including medicine, construction, sewage disposal, cosmetics, coating materials aircrafts etc. Our future plan is to:

- Analyze the DSC results of remaining series of nanocomposites.
- To characterize nanocomposites by TGA & DMTA
- Synthesis of ZnO nanocomposites by using silane coupling agent.
- Hybrid ZnO/TiO<sub>2</sub> nanocomposites will be synthesized.

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