

Final Report of the project

**Investigation of the Impact of ZnO Nanoparticles on the Properties of a  
Difunctional Epoxy Resin**

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## Introduction

Epoxy resins (ERs), which is a class of versatile thermosetting polymers, has been developed rapidly since invented, are widely used for a variety of applications [1]. Epoxy resins are used in insulation such as electrical machinery, in power electronic devices, packing of integrated circuits, electronic, wear resistance and light-emitting diode (LED) due to the small volume shrinkage in curing and outstanding electrical performance. They are also employed as coatings and adhesives because of their good mechanical properties and strength of interaction with materials and metals, respectively. The properties of these resins can be varied by changing the curing conditions. Multitudes of curing agents are available for curing these materials. The optimum properties for a particular application are achieved through the proper selection of curing agent and curing conditions. However, cured epoxy resins are brittle. The toughness and other mechanical properties can be improved by blending with rubber, thermoplastics, inorganic fillers and nanoparticles [2-9].

Modification of epoxy resins is still necessary since some application in the engineering area require higher thermal and mechanical properties. One of the major applications of epoxy-based thermosetting polymers is in the protective coating industry. Epoxy powder coatings are most widely used owing to their distinguished corrosion, dielectric, and mechanical properties. However, the main drawback of these materials is weak toughness. So, toughness improvement of the epoxy coating is crucial. Many materials like rubber elastomer, thermoplastics, liquid crystalline epoxy, micro and nanoparticles etc. are used to improve its toughness [10-13]. An effective approach to enhance thermophysical properties of epoxy resins is introducing various inorganic nanoparticles into the polymer matrix. Ability to control good dispersion of particles in polymers is one key challenges to overcome for achieving optimal performance of these inorganic/polymer hybrids. The development of high performance materials based on epoxy resin is finding a growing number of applications where high thermal stability and environmental resistance combines with a good tribological performance.

ZnO is a self-activated crystal of hexagonal wurtzite structure with direct wide band gap energy of 3.37 eV at room temperature [14,15], and has strong excitonic emission in the ultraviolet range even at room temperature due to its large exciton binding energy of 60 meV which is significantly larger than other materials [16]. ZnO has wide application in various fields, such as short-wavelength light-emitting diode and room temperature UV lasing diode, field emission display, gas sensors and catalyst [17–21]. Epoxy resins are used as shields for LEDs. It is necessary to have good mechanical and thermal properties for this application. Therefore ZnO is a potential modifier for epoxy resin. Epoxy resin can be easily processed and the ultimate

properties can be controlled by proper choice of curing agent and curing conditions. Also the inorganic filler can improve the tribological properties of the resin.

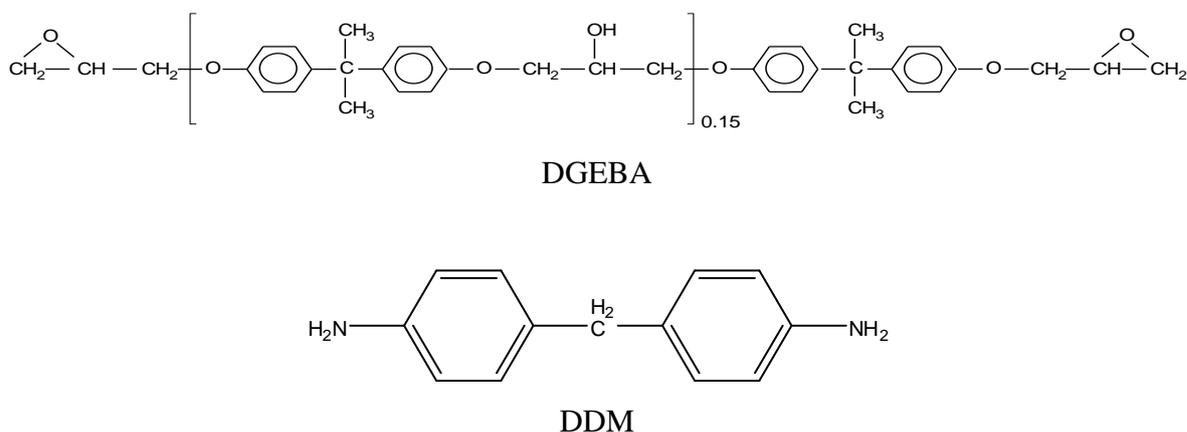
Epoxy resin is modified using various inorganic fillers of micro and nano size. Li et al [22] reported a transparent ZnO/epoxy nanocomposite with high-UV shielding efficiency. They used a difunctional epoxy resin for preparing the composite. Transparent ZnO/epoxy nanocomposites were prepared via in situ polymerization. ZnO nanoparticles with an average size of 26.7nm gave the optimal optical properties. Smaoui et al [23] investigated the dielectric relaxations of an epoxy resin matrix and epoxy nanocomposites made by dispersing conductive nanoparticles (ZnO and Zn 97% OAl 3%) in the epoxy matrix were investigated by means of DRS and TSDC techniques. It was found that the distribution of relaxation times associated with the interfacial process becomes asymmetric in nanocomposites. In the low frequency range conductivity is governed by charges carriers of the epoxy matrix rather, than of the nano-fillers.

The preparation of ZnO/epoxy composites with homogeneous dispersion were reported by Ding et al [24]. The investigation showed that the composite containing 5 wt% of ZnO particles (about 100–200 nm) had the optimal mechanical properties. The curing, thermal degradation kinetics and mechanical properties of epoxy resin based on the diglycidyl ether of bisphenol-A and 2,2'-diamino-1,1'-binaphthalene as a hardener and ZnO as a nanofiller were investigated. The higher thermal and mechanical properties were obtained with the addition of 5 phr of ZnO nanoparticles. The addition of ZnO nanoparticles into the epoxy matrix resulted in a significant increment in the thermal stability and activation energy of thermal degradation. The epoxy nanocomposite exhibited an increase in storage modulus and glass transition temperature compared to the neat epoxy.

The intrinsic brittle nature of epoxy resin makes it necessary to incorporate additives to improve its toughness. Among the various epoxy resins, the difunctional epoxy resin was found to be easily processable and cost effective. Rubber, thermoplastic, inorganic fillers and nano sized particle can be used to improve the properties of epoxy resin. Nano particle are much efficient in improving the ultimate properties of the resin. In present work ZnO will be used to improve the properties of a diglycidyl ether of bisphenol-A based epoxy resin. ZnO has wide application in various fields, such as short-wavelength light-emitting diode and room temperature UV lasing diode, field emission display, gas sensors and catalyst and epoxy resin is used for electrical and electronic applications. A combination of both will result in material with good properties.

## **Experimental**

High purity of zinc sulphate (Merck) and ammonium bicarbonate (Merck) were used for synthesis of ZnO nanoparticles. The epoxy resin used was general purpose medium viscosity laminating resin based on diglycidyl ether of bisphenol-A with an epoxide equivalent weight of 185. The curing agent used was 4, 4'-diaminodiphenyl methane (DDM) with a melting point of 175°C and molecular weight of 243.31g/mol. The chemical structures of DGEBA and DDM are shown in the Fig. 2.1.



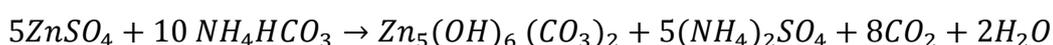
**Figure 2.1** Chemical structures of DGEBA and DDS

Stoichiometric ratio of curing agent was used for curing epoxy resin. The amount of curing agent required for epoxy resin was calculated using the equation

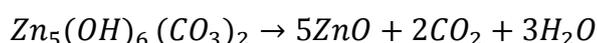
$$\left( \frac{\text{molecular weight of polyamine}}{\text{number of active hydrogens}} \div \text{weight per epoxide} \right) \times 100 = \text{parts by weight of polyamine per 100 parts by weight of resin}$$

### Preparation of ZnO nanoparticles

Zinc sulphate (1.5 mol/L) and Ammonium bicarbonate (2.5 mol/L) were prepared in distilled water and 126 ml  $\text{NH}_4\text{HCO}_3$  solution was added to 100 ml  $\text{ZnSO}_4$  solution while stirring and the reaction mixture was kept at 45°C. The slurry of basic zinc carbonate (BZC) in the form of white precipitate was obtained. It was then filtered washed and dried. Finally zinc oxide nanoparticles were prepared by calcining the precipitate at 500 °C for 1 hour. In this process, the reaction of Zn ions and ammonium acid carbonate proceeds according to the following equation



The precipitate was filtered, washed free of sulphate and dried. Finally Zinc oxide nanoparticle was prepared by calcining the precipitate at 500°C for 1hour.



### Preparation of nanocomposite

Epoxy resin- ZnO nanocomposites were prepared using magnetic stirring. Composites with 1, 2 and 3 phrZnO were prepared. Required amount of ZnO is weighed out into a 250 mL beaker and 40 g of epoxy resin is weighed out into it. ZnO was dispersed in epoxy resin using an

overhead stirrer for half an hour. Stoichiometric amount of DDM was added to the ZnO epoxy dispersion. DDM was completely dissolved at 120°C with constant stirring. The mixture was degassed under vacuum at 120°C for 15 minutes. After degassing the mixture was poured on a stainless steel mould kept at 120°C in an air oven. A thin layer of mould releasing agent was applied on the mould to prevent adhesion of the composite to the mould. The samples were cured at 120°C for 3 hours and post cured at 180°C for 1 hour. Specimens of required size were cut from the cured sheets for characterization. A neat epoxy resin laminate was prepared without ZnO in a similar manner.

#### *Fourier transform infrared spectroscopy*

Samples were scanned for characteristic absorptions using a Perkin Elmer Spectrum GXA fourier transform infrared (FTIR) spectrometer in the range 4000 – 400cm<sup>-1</sup>. The instrument employed a pyroelectric detector, which scanned the samples in the form of KBr pellets.

#### *X-ray powder diffraction*

X-ray powder diffraction (XRD) was used to characterize the zinc oxide powders. Particle size of the samples was determined using X-ray diffraction technique. XRD patterns were collected using Bruker, D8 advance diffractometer using Cu K $\alpha$  radiation.

#### *Transmission electron microscopy*

The morphology and particle size of zinc oxide were observed using transmission electron microscope (TEM). Transmission electron micrograph of ZnO samples was performed with a transmission electron microscope Model JEM 2100.

#### *Tensile Properties*

Tensile properties were determined according to ASTM D638 using dumbbell shaped specimens. The measurements were done using a universal testing machine (TINIUS OLSEN H50KT) at a cross head speed of 10mm/min at room temperature. Tensile strength was calculated using equation

$$\text{Tensile strength} = \frac{P}{bd}$$

Tensile strength was calculated using the equation given below

$$\text{Tensile strength} = \frac{P}{bd}$$

where, P is the load at failure

b is the width of the specimen and

d is the thickness of the specimen

Tensile modulus was taken as the initial slope of the stress-strain curve.

#### *Fracture Toughness*

Fracture toughness of the specimens was determined according to ASTM STP410. Rectangular specimens of 100mm length, 35mm width and 5mm thickness were used for fracture toughness measurements. A notch of 5mm was made at one edge of the specimen. A natural crack was made by pressing a fresh razor blade into the notch. The analysis was done in tension mode. The fracture toughness expressed as stress intensity factor ( $K_{Ic}$ ) was calculated using equation,

$$\text{Stress intensity factor, } K_{Ic} = \frac{QPa^{1/2}}{bd}$$

where P is the load at the initiation of crack

a is the crack length

b is the breadth of the specimen and

d is the thickness of the specimen and

Q is a geometry constant

Q is calculated using the following equation.

$$Q = 1.99 - 0.41(a/b) + 18.7(a/b)^2 - 38.48(a/b)^3 + 53.85(a/b)^4$$

#### *Glass transition temperature*

The  $T_g$  of the nanocomposite was determined using TA Instruments DSC 2920. In order to determine the  $T_g$  the samples were heated to 250°C at 10°C/min in nitrogen atmosphere.

#### **Characterization of ZnO**

Weighed out accurately about 1.5g of ZnO and 2.5g of ammonium chloride. Dissolved this in 50 ml of standard hydrochloric acid (1N) and titrated the excess of acid with standard sodium hydroxide solution (1N) using methyl orange as indicator. A blank determination was done without using the material. Purity of zinc oxide is calculated using equation 1.<sup>1</sup>

$$\text{Zinc oxide, percent by mass} = 4.07 (B-A) / M \dots\dots\dots (1)$$

Where, B = Volume in ml of standard sodium hydroxide solution used in the blank determination.

A = Volume in ml of standard sodium hydroxide solution used in the titration with the material

M = mass in g of the material taken for the test

The ZnO samples were found to be 99.8% pure from the analysis.

#### **Fourier transform infrared spectroscopy**

The FTIR spectrum of ZnO particles is shown in Fig.1. The peak at 400  $\text{cm}^{-1}$  shows the distinct stretching vibration of zinc oxide.

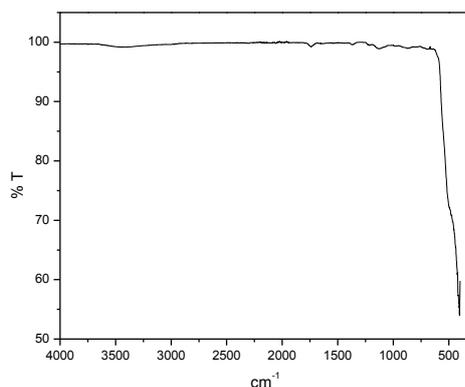


Figure 1 FTIR spectrum of ZnO

### X-ray powder diffraction

X-ray powder diffraction (XRD) was used to characterize the zinc oxide powder. Crystallite size is calculated using Scherrer equation.

$$CS = 0.9\lambda/\beta\cos\theta$$

where, CS is the crystallite size

$\beta$  is full width at half maximum (FWHM) of an hkl peak at  $\theta$  value.

Figure 2 shows the XRD pattern of ZnO particles. It is very clear from the figure that the major reflections between  $30^\circ$  and  $40^\circ$  ( $2\theta$  values) indicate more crystalline regions in the zinc oxide sample. Also the less intense peaks at  $47^\circ$ ,  $57^\circ$ ,  $62^\circ$  and  $68^\circ$  ( $2\theta$  values) indicate the high crystallinity of ZnO samples. The crystallite size of the ZnO samples was calculated using Scherrer's formula. The crystallite size for zinc oxide was found to be 15nm.

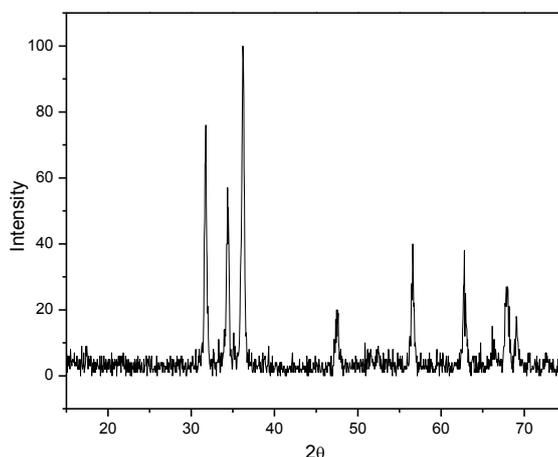


Figure 2 X-ray diffraction pattern of ZnO particle

### Transmission electron microscopy

The morphology and particle size of zinc oxide were observed using transmission electron microscope (TEM). Figure 3 shows the TEM image of zinc oxide prepared by precipitation method. It shows that ZnO particle size prepared by precipitation method have an average particle size of 50 nm.

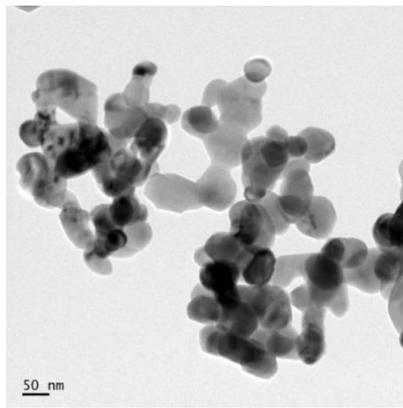


Figure 3 Transmission electron microscopic image of ZnO particle

### Tensile properties

The tensile strength and Young's modulus of the composites are summarised in Table 1. No yielding was observed in the tensile stress-strain curves of DDM cured epoxy resin and nanocomposites.

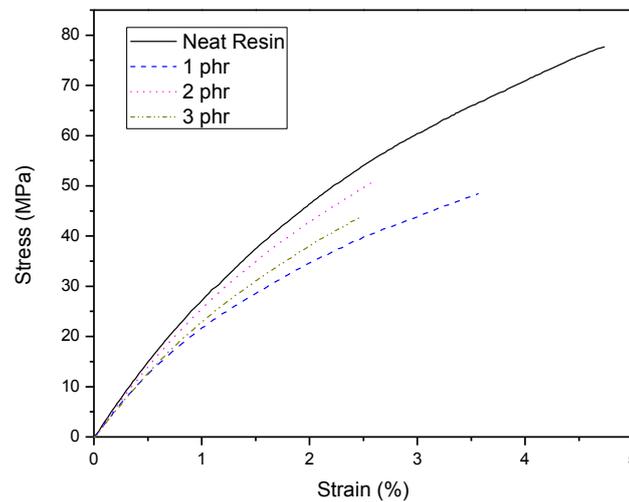


Figure 4 Tensile stress-strain curves of nanocomposites

The tensile strength of the composites decreased with increase in ZnO content. The composites with 3phr ZnO showed the maximum decrease. The modulus of nanocomposites remained the same as that of the neat epoxy resin. The Young's modulus decreased slightly with increase in ZnO content.

ZnO content (phr)	Tensile strength (MPa)	Young's modulus (GPa)
0	77.7	3.2
1	48.5	2.8
2	50.6	3.1
3	46.6	3.1

Table 1 Tensile property of DGEBA/ZnO nanocomposites

### Flexural properties

The flexural properties of the composites are given in Table 2. The flexural strength of the composites decreased slightly with increase in ZnO content. The composites with 3phr ZnO showed the maximum decrease. The flexuareal modulus decreased with increase in ZnO content.

ZnO content (phr)	Flexural strength (MPa)	Flexural modulus (GPa)
0	112	1.9
1	108	1.8
2	109	1.8
3	105	1.6

Table 2 Flexural properties of DGEBA/ZnO nanocomposites

### Fracture toughness

Fracture toughness is the resistance of a material towards crack initiation and propagation. To increase the toughness of a material, it is necessary to improve the ability of the system to absorb the energy responsible for crack propagation. The energy could be external or internal or both. The most common method to increase fracture toughness of epoxy resin was to incorporate one or more modifiers into the epoxy resin. The fracture toughness was expressed as critical stress intensity factor ( $K_{Ic}$ ). The fracture toughness of epoxy resin modified with ZnO is summarised in Table 3.

ZnO content (phr)	$K_{Ic}$ ( $MNm^{-3/2}$ )
0	3.96
1	3.93
2	4.25
3	3.19

Table 3 Fracture toughness of DGEBA/ZnO nanocomposites

It is observed that failure loads increase with an increase in the nanoZnO content. But only the addition of 2phr ZnO showed a slight increase in fracture toughness. The increase in the fracture surface area due to crack deflection is the major toughening mechanism.

### Glass transition temperature

The glass transition temperature of the composites is shown in the table. It was found that the addition of ZnO did not affect the glass transition temperature of epoxy resin.

ZnO content (phr)	T <sub>g</sub> (°C)
0	172
1	175
2	173
3	170

Table 2 T<sub>g</sub> of DGEBA/ZnO nanocomposites

## Conclusions

Nano zinc oxide particles were prepared successfully by precipitation method in good yield. The prepared samples are found to more than 99% pure. The FTIR spectrum showed characteristic peak between 400 and 450cm<sup>-1</sup>. The nanoparticles have an average size of 50nm from TEM analysis. The tensile properties of the nanocomposites were investigated according to ASTM standards. The tensile strength decreased with increase in ZnO content. The Young's modulus showed a mild decrease. The results showed that zinc oxide is not a good modifier for epoxy resin. The fracture toughness of the nanocomposites showed mixed response. Addition of 2phr ZnO slightly increased the fracture toughness. The increase fracture surface area is responsible for the increase in fracture toughness and the fracture surface looked rougher in the case of 2phr ZnO sample. The lack of uniform dispersion above 2phr addition may be responsible for the decrease in fracture toughness. The glass transition temperature of the composites remained unchanged even after the addition of ZnO nanoparticles.

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