

Effect of Zinc Oxide Nanoparticles on Mechanical Properties of Diglycidyl Ether of Bisphenol-A

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Abstract

This study reports on the synthesis of zinc oxide (ZnO) nanostructures and examines the performance of polymer nanocomposites fabricated using ZnO dispersed in polymer host matrices. The polymer matrix used was an epoxy based thermosetting polymer known as Diglycidyl Ether of Bisphenol-A (DGEBA). Zinc oxide nano particles were prepared by precipitation method using Poly Vinyl Alcohol as the surface modifier. It was characterized using Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD). And the average particle size has been found to be 25 nm. The main objective of this study is to investigate the simultaneous effect of the additive ZnO nanoparticles and curing agent on the curing kinetics, mechanical and morphological properties of Diglycidyl ether of bisphenol-A system. The mechanical properties of epoxy resin based on diglycidyl ether of bisphenol-A and Zinc Oxide were also investigated and improved mechanical properties were obtained for epoxy resin with 2% filler concentration.

Keywords: Zinc oxide nanoparticles; Epoxy nanocomposites; Mechanical properties

Introduction

The idea of nanotechnology was introduced in 1959, when Richard Feynman gave a talk called "There is Plenty of Room at the Bottom" Though he never explicitly mentioned nanotechnology, he suggested that it will eventually be possible to precisely manipulate atoms and molecules. Later the emergence of nanotechnology in the 1980's was caused by the convergence of experimental advances such as the invention of the scanning tunneling microscope in 1981 and the discovery of fullerenes in 1985 [1-3].

Nanoscience and technology are widely cited to be the defining technology for 21st century. The most suitable definition for nanotechnology is that the control and manipulation of matter at nano dimensions roughly 1 to 100 nm. Encompassing nano scale science, engineering and technology, nanotechnology involves imaging, measuring, modelling, and manipulating matter at this scale. At the Nano scale, the physical, chemical, biological properties of materials differ in fundamental and valuable ways from the properties of individual atoms and molecules or bulk matter. Nanotechnology research is directed towards the understanding and creating improved materials, devices, and systems that exploit these new properties. The introduction of nanotechnology resulted in development of Nano powders that can be used for wide range of applications. Research has been made for nano-size materials in recent years because of their unique character differing from those in the bulk state. One of the great promises that nanoparticles of metal oxides hold in chemical applications is their remarkable ability to chemically absorb a wide variety of molecules, especially organic molecules that are concern as environmental hazards [4-7].

Zinc oxide, with its unique physical and chemical properties, such as high chemical stability, high electrochemical coupling coefficient, broad range of radiation absorption and high photo stability, is a multifunctional material in materials science, zinc oxide is classified as a semiconductor in group II-VI, whose covalence is on the boundary between ionic and covalent semiconductors. A broad energy band (3.37 eV), high bond energy (60 meV) and high thermal and mechanical stability at room temperature make it attractive for potential use in electronics, optoelectronics and laser technology. The

piezo- and pyroelectric properties of ZnO mean that it can be used as a sensor, converter, energy generator and photo catalyst in hydrogen production. Because of its hardness, rigidity and piezoelectric constant it is an important material in the ceramics industry, while its low toxicity, biocompatibility and biodegradability make it a material of interest for biomedicine and in pro-ecological systems [8,9].

The variety of structures of Nano metric zinc oxide means that ZnO can be classified among new materials with potential applications in many fields of nanotechnology. Zinc oxide can occur in one- (1D), two- (2D), and three-dimensional (3D) structures. One dimensional structure make up the largest group, including nano rods, -needles, -helixes, -springs and -rings, -ribbons, -tubes -belts -wires and -combs. Zinc oxide can be obtained in 2D structures, such as Nano plate/Nano sheet and Nano pellets. Examples of 3D structures of zinc oxide include flower, dandelion, snowflakes, coniferous urchin-like, ZnO provides one of the greatest assortments of varied particle structures among all known materials [10,11].

Zinc oxide nanoparticles possess various remarkable physical and chemical properties that are distinct from those of conventional bulk materials. It is one of the most promising material for its wide range of applications in sensors, field emission, light emitting diodes, dye-sensitized solar cells, photo induced switching devices, Variastors and photocatalytic activity. Zinc oxide can be synthesized in many ways including sol-gel method, mechano chemical processing, spray dying, pyrolysis, controlled precipitation, micro emulsion synthesis, hydro thermal processing, self-assembling, vapour transport process.

Nanocomposites are composites in which at least one of the phases

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Received September 27, 2016; Accepted October 28, 2016; Published November 08, 2016

Citation: Mohan AC, Renjanadevi B (2016) Effect of Zinc Oxide Nanoparticles on Mechanical Properties of Diglycidyl Ether of Bisphenol-A. J Material Sci Eng 5: 291. doi:10.4172/2169-0022.1000291

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shows dimensions in the nanometre range. These are high performance materials that exhibit unusual property combinations and unique design possibilities and are thought of as the materials of the 21st century. With an estimated annual growth rate of about 25% and huge demand for engineering polymers, their potential is so promising that they are useful in several applications ranging from packaging to bio-medical. Almost all types of polymers, such as thermoplastics, thermosets and elastomers have been used to make polymer nanocomposites. A range of Nano reinforcements with different shapes have been used in making polymer nanocomposites [12,13].

Novel properties of nanocomposites can be obtained by successfully joined characteristics of parent constituents in a single material. These materials are different as both materials like pure polymers and inorganic nanoparticles with some physical and chemical properties. With the addition of nanosized inorganic particles into polymer matrices the new composites material will exhibit unexpected properties which greatly different from that of conventional materials.

Experimental

Materials

For the preparation of zinc oxide nano particles two different precursors were used. First one is zinc sulphate heptahydrate ($M=287.49$ g/mol, Sigma Aldrich), and zinc acetate ($M=219.5$ g/mol, Merk), Poly Vinyl Alcohol (PVA) was used as the surface modificant. For the preparation of the nanocomposites the polymer matrix selected was an epoxy based thermosetting polymer which is known as diglycidyl ether of bisphenol-A and it is commercially known as DER 332 from sigma Aldrich company with an epoxy equivalent weight of 175 g/eq. the hardener used is an aliphatic amine based and it is commercially known as Ch301.

Sample preparation

Preparation using zinc sulphate as the starting material: To the aqueous solution of zinc sulphate heptahydrate sodium hydroxide was added drop wise in a molar ratio of 1:2, under vigorous stirring, and the stirring action is continued for almost 18 hours and large amount of white precipitate was formed, this precipitate was filtered and washed with distilled water and dried using a muffle furnace at a temperature of 100°C and it is ground to fine powders and finally the powder obtained was calcined at different temperatures such as 500°C , 700°C , 900°C [14,15]. Here the particles are calcined at different temperatures in order to obtain the relation between yield and temperature. It was found that as the calcination temperature increases the yield decreases.

Preparation using zinc acetate as the starting material: Initially 1 M zinc acetate solution was stirred vigorously, and to this vigorously stirred zinc acetate, 2 M sodium hydroxide solution was added drop wise, large amount of white slurry's were formed, and this white slurry were continuously stirred for 18 hours [16]. A white precipitate was formed, which was filtered and washed with distilled water and dried using muffle furnace, ground to fine powder and finally calcined at 400°C . If the temperature is more than 400°C then the particles starts to thermally degrade. A noticeable colour change from white to a dark ash colour also occurs.

Preparation using Poly Vinyl Alcohol (PVA) as surfactant: To prepare zinc oxide nanoparticles 0.01% PVA solution prepared initially and 2 ml PVA was added to zinc sulphate heptahydrate solution and sodium hydroxide was added to it drop wise very slowly. The resulting solution was stirred for almost 18 hours. After 18 hours large amount

of white precipitate was formed which was filtered and washed with distilled water and dried in a muffle furnace at a temperature of 100°C for 2 hours. Then it was ground to fine powders and finally calcined at 450°C [17,18].

To prepare the nanocomposites a specific amount of zinc oxide nanoparticles were added into the polymer matrix. The amount of epoxy resin selected was 10 g and the amount of hardener was 1 g i.e., 10% of the polymer matrix. In a series of experiments the amount of zinc oxide selected was 1, 1.5, 2, 3, 4, 5, 10 percentage based on the weight of the resin/hardener system. An ultrasonic mixing process was employed for the dispersion of particles in the polymer matrix and it was achieved by using a sonicator. The mixture was sonicated for almost 6 hours [19,20].

Measurements

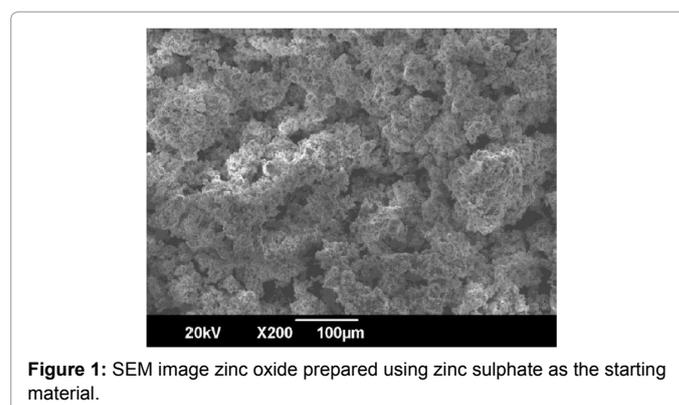
Scanning Electron Microscopy (SEM) images of the zinc oxide nanoparticles and the epoxy nanocomposites were obtained using a JSM-JEOL 6390 Scanning Electron Microscope. The JSM-6390 is a high performance, low cost scanning electron microscope with a high resolution of 3 nm. The customizable graphical user interface allows the instrument to be intuitively operated. It is equipped with an auto coater for coating the samples and the coating time is automatically adjusted by the coater and it varies according to the nature of the sample [21].

Mechanical properties of the samples were tested using Universal Testing Machine (UTM). And Shimadzu's AGS-X was used. Shimadzu's AGS-X series of universal testers combines advanced specifications with a cost-effective, modern design. By incorporating multiple control options, load cells with maximum capacities from 1 N (0.22 lbf) to 300 KN (66,000 lbf), and the utmost in safety considerations, the AGS-X series delivers practical testing solutions. The enhanced features of the autograph AGS-X series testers allow for easier and more efficient testing. It is equipped with an adjustable main operation panel for conveniently developing and storing conditions and performing tests without having connected to be a PC.

Results and Discussions

Scanning electron microscopy (SEM)

Figure 1 shows the Scanning Electron Microscope (SEM) image of the zinc oxide nanoparticles under lower magnification and it shows that the particles are agglomerated and complete separation is not occurred. It is seen that the particles are held together because of weak physical forces. Here particles were formed with size in the micron range. Hence zinc oxide prepared using zinc sulphate as the starting material does not produce particles with size in the nanometre range

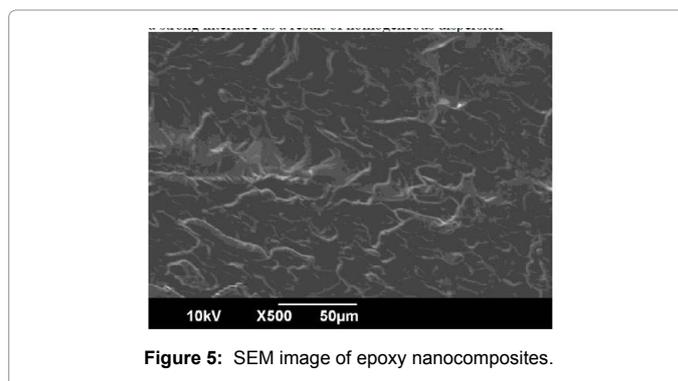
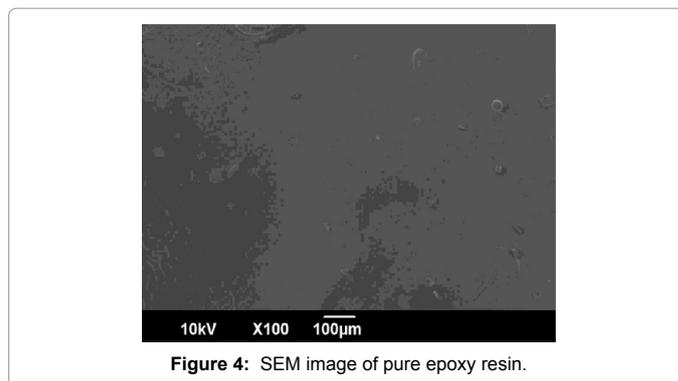


and the particle separation is also not good. This method of preparation was highly affected by particle agglomeration [22].

Figure 2 shows the Scanning Electron Microscope (SEM) image of zinc oxide prepared using zinc acetate as the starting material under lower magnification. Here the agglomeration of particles is marginal. But the particle separation is not good enough. Here also we can see that the particles are held together by weak physical forces it clearly suggests that particle separation is not good enough and also particles with size in micron range was formed. It indicates that the zinc oxide prepared using zinc acetate as the starting material does not produce particles with size in the nanometer range and the particle agglomeration is less compared to the previous method [20,21].

Figure 3 shows the Scanning Electron Microscope image of zinc oxide prepared using zinc sulphate as the starting material and Poly Vinyl Alcohol as the surfactant. Here the negative impact of particle agglomeration and particle separation was sorted out to an extent due to the introduction of Poly Vinyl Alcohol as surfactant. Here the particle agglomeration is very less and we can see that particles with size less than 100 nm were formed. This gives a clear idea about the particle separation, we can see that the particles are separated smoothly and not affected by agglomeration. So these particles are good enough for the preparation of polymer nanocomposites [23].

In order to take advantage of nanoscale reinforcement and to obtain desired properties, a good dispersion of nanofiller is crucial. Figure 4 shows the SEM image of the pure epoxy resin. The pure epoxy resin exhibits a relatively smooth surface. Figure 5 shows the SEM images of the nanocomposites. It is evident that the nanocomposite has a surface morphology indicating both individual and dispersion packing of zinc oxide nanoparticles. Both Figures 4 and 5 shows the interaction between the polymer matrix and zinc oxide nanoparticles and point out the strong adhesion between the organic and inorganic



phases and this interaction leads to good wetting and a strong interface as a result of homogeneous dispersion.

The nanocomposites have a rougher fracture surface demonstrating increased surface roughness as a result of addition of zinc oxide nanoparticles. ZnO nanoparticles are apparently dispersed homogeneously in composite and they are prevented from the agglomeration due to the high viscosity of the epoxy matrix.

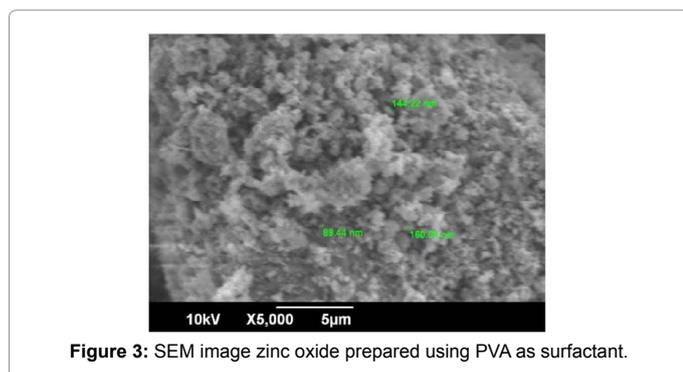
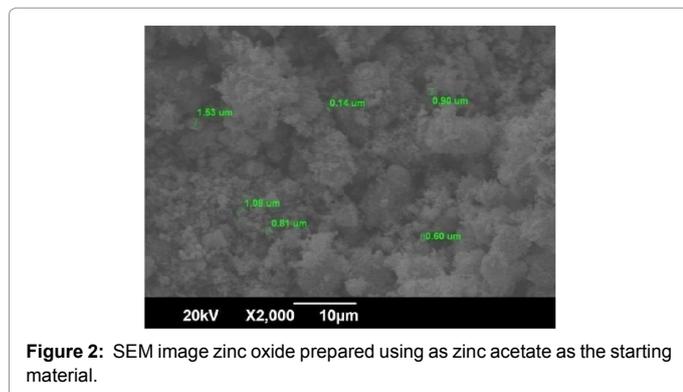
X-ray diffraction (XRD)

The XRD of the synthesized zinc oxide shows broad peaks at values of 31.9, 34.5, 36.3, 56.7, and 62.9 which are typical for the zinc oxide structure. Notable line broadening of the diffraction peaks is an indication that the synthesized materials are in nanometer range. The average particle size has been determined from full width at half maximum (FWHM) of the diffraction peaks using Scherrer's equation. The particle size of zinc oxide nanoparticles has been found to be 24.96 nm (Figure 6) [24].

Mechanical properties- tensile strength

ASTM standard, D 638, was used for the determination of the tensile strength or mechanical strength of the pure epoxy resin and zinc oxide-epoxy nanocomposite. The mechanical properties of the nanocomposites were tested using Universal Testing Machine (UTM). Mainly tensile strength of the composites and pure resin are tested using this method. And the results are tabulated below.

From the Table 1 it's clear that the composites exhibit good tensile strength improvements at lower composition. The pure epoxy resin has a tensile strength of 14.3 N/mm² whereas the composite with a filler concentration of 2% exhibit a tensile strength of 29.7 N/mm² i.e., more than double. Which means the dispersion of particle is good under lower concentration and it leads to good improvement in mechanical properties of the composites. But at higher filler concentration the



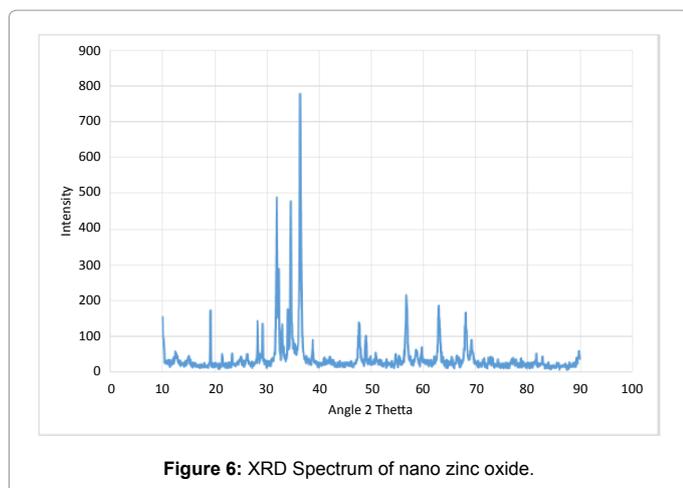


Figure 6: XRD Spectrum of nano zinc oxide.

Composition (%)	Tensile Strength (N/mm ²)	Breaking Force (N)
0	14.3	558.5
1	16.3	637.9
1.5	23	897
2	29	1161.2
3	15.5	605.5
5	10.4	409

Table 1: Data from the analysis of UTM measurements at different compositions.

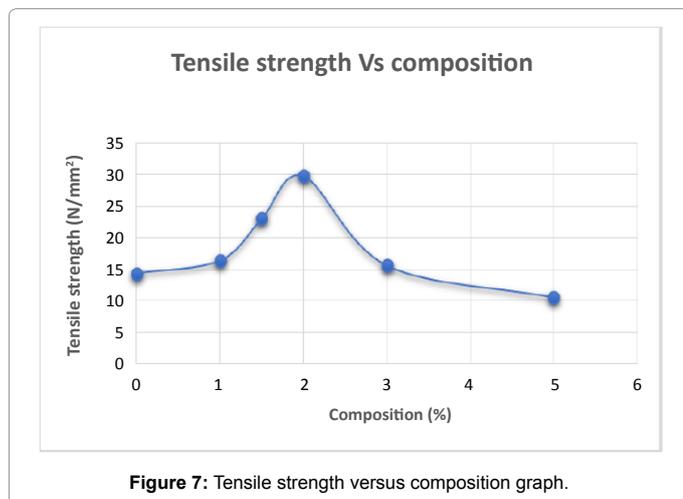


Figure 7: Tensile strength versus composition graph.

tensile strength actually decreases. This may be because of the poor dispersion of the particles in the resin. At low filler concentration or at situation where inter-filler interaction is not favorable over filler-polymer interaction, the mechanical hardening can occur. At higher filler concentration, filler molecules are more prone to interact with each other compared to the polymer molecules leading to percolated tunnel of interacting fillers. As a result, the onset of softening or reduction in modulus occurs. The interface between the fillers and the matrix is also important. At higher concentration this interface is weak and it would have stress concentration, then the generation of cracks. So the weak interface would lead to a lower strength and also a lower strain at break.

Figure 7 shows the variation of tensile strength with composition. From this graph we can see that at 2% and 1.5% filler concentration the tensile strength value is very high compared to other compositions

which means the dispersion is good at lower composition and it leads to mechanical property improvements [23,25].

Conclusions

Zinc oxide nanoparticles were successfully prepared using Poly Vinyl Alcohol as the surfactant and the prepared nano powder was characterized using Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). According to the XRD characterization the average particle size has been determined using Scherrer's equation. The average particle size of zinc oxide nanoparticles has been found to be 24.96 nm and that's good enough for the preparation of polymer nanocomposites. The polymer matrix selected for the preparation of nanocomposites was an epoxy based thermosetting polymer known as diglycidyl ether of bisphenol-A (DGEBA) which is commercially known as Dow Epoxy Resin 332 (DER332). In order to obtain a desirable dispersion of ZnO nanoparticles in the resin matrix, an ultrasonic treatment was used. Images from SEM measurements revealed that the used dispersion method was reliable.

The tensile strength of the nanocomposites were tested using UTM analysis and epoxy resin with 2% zinc oxide showed good mechanical strength improvements i.e., the tensile strength of the nanocomposite was doubled to that of the pure epoxy at this particular composition.

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