

Green Synthesis of Zirconia (ZrO₂) Nanoparticles Using *Curcuma Longa* Extract and Investigation of Compressive Strength of Epoxy Resin (EP)/ZrO₂ Nanocomposites

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Abstract

Zirconia (ZrO₂) nanoparticles are polymorphic materials having a wide range of applications. It can be synthesized via green as well as chemical synthesis methods. In this work, ZrO₂ nanoparticles were synthesized by the green method using *Curcuma longa* extract. *Curcuma longa* extract was prepared using the standard method. The synthesized ZrO₂ was characterized by the X-ray diffraction (XRD) analysis and Fourier transform infrared (FTIR) spectroscopy for their structural and size analysis. The analysis of the XRD pattern of ZrO₂ showed the tetragonal phase structure and the size was calculated using the Debye Scherrer equation which was about 35 nm. The FTIR spectra analysis showed a broad absorption peak particularly at about 774 cm⁻¹ and about 499 cm⁻¹ correspondings to Zr-O₂-Zr asymmetric and Zr-O stretching modes, respectively. The characterized ZrO₂ nanoparticles were used for the preparation of epoxy resin/ZrO₂ nanocomposites. The compressive strength of pure epoxy resin and epoxy resin/ZrO₂ nanocomposites were measured by a compressive strength tester and the result indicates the high amount of zirconia showed the less compressive strength in nanocomposites.

Keywords: Zirconia, green synthesis, epoxy resin, compressive strength, nanocomposite

Introduction

Nanotechnology is employed for the assembly, manipulation, and use of materials ranging in nanometers [1,2]. Nanomaterials are one in the entire foremost component of the nanotechnology and wide class of materials that has particulate substances which have one dimension from 1 to 100 nm in size [3]. There are several kinds of nanoparticles such as metal, semi-conductor, and bio, out of those nanoparticles, zirconia (ZrO₂) is polymorphic, and advanced ceramic material having useful optical, electrical, thermal, hardness, and other characteristics. Its molar mass is 231.891 g/mol, the freezing point is 2715°C and the boiling point is 4300°C [4].

It is further employed in different industries as a refractory material, cutting tools, limit coating, catalyst support, sensors, fuel cells, optical devices, metallic glasses [5]. ZrO₂ exists in three crystal phases *i.e.* monoclinic phase is clinically stable at gas pressure, the tetragonal phase exists within the temperature range of 1100-2370°C and therefore the cubic phase is found above 2370°C. When it is used

at the elevated temperature and cooled to the area temperature, the quantity expansion occurs from cubic to tetragonal. This volume change causes large stress that results in cracking. Thus, bulk zirconia cannot be used at elevated temperatures [6].

Zirconia nanoparticles will be synthesized employing various methods like sol-gel [7], combustion [8], hydrothermal [9], co-precipitation [10], and green [11]. The green method is greatly employed in synthesizing the nanoparticles using plant extract using from leaves, roots, barks, etc. [11]. The extract may contain the reducing agent and some compounds act as a capping agent such as flavonoids, terpenoids, reducing sugars, etc. [12].

Likewise, Zirconia nanoparticles are used as fillers in polymeric nanocomposites to boost their strength and stiffness. However, because of the high aggregation tendency of nanoparticles, structural defects occur in nanocomposites, leading to a decreased possibility of mechanical property improvement [13]. Liquid epoxy resin is employed as structural adhesives and coating material because of its low cost, good workability, volatile compound free eco-friendliness,

good adhesion, heat resistance electrical insulation, chemical resistance, and weather resistance. However, the most epoxy resin needs additional fillers to improvise mechanical and thermal properties thanks to their inherent brittleness and industrial requirement. Zirconia nanoparticles are used as fillers to enhance their strength and stiffness. Organic modifiers are accustomed to progress interfacial bonding between fillers and resin [14].

Polymer nanocomposite (PNC) comprises polymer or copolymer with nanoparticles or nanofillers dispersed in the polymer matrix. The PNC's belong to the category of the multiple-phase system (MPS). These systems require controlled mixing, stabilization of achieved dispersion, the orientation of phase, and compounding strategies for all MPS including PNC [15]. Microhardness property was improved in epoxy resin/SBS/layered silicate (LS) and boehmite nanocomposite due to dispersion of layered silicate and boehmite nanofillers [16]. Recently, it was found that the introduction of inorganic nanoparticles to polymeric adhesives at a low percentage may cause the advance of shear resistance of structural joints. Only some studies of epoxy-ZrO₂ composites associated with their morphology and mechanical properties are reported and that they show that the mechanical resistance and toughness of synthetic resin are improved by increasing the content of ZrO₂ nanoparticles. This can be attributed to the fact that ZrO₂ nanoparticles have a way higher strength than epoxy matrix alone and to the nice bonding between filler and matrix [17]. In this paper, the herbaceous plant extract is employed for the synthesis of zirconia nanoparticles, and therefore the compressive strength of epoxy resin (EP)/ZrO₂ nanocomposites is discussed for mechanical purposes.

Materials and Methods

a. Materials

Curcuma longa was collected from the local market and grinded to a fine powder for the preparation of its extract. Zirconyl chloride octahydrate (ZrOCl₂.8H₂O), (98% purity) was manufactured by LOBA Chemie Pvt. Ltd, Mumbai, India. Epoxy and hardener were marketed from a local supplier in Kathmandu. All the reagents used were of analytical grades and used without further purification.

b. Methods

Preparation of *Curcuma longa* extract

About 20 g of turmeric powder was weighed and kept in a 500 mL beaker. 200 mL of water was added to

it. Then the mixture was boiled for a half-hour with continuous stirring by a magnetic stirrer. Then the boiled mixture was filtered carefully and therefore the resulting filtrate was the extract.

Synthesis of Zirconia nanoparticles

About 50 mL of 0.1 M zirconyl chloride octahydrate [ZrOCl₂.8H₂O] was taken in a 250 mL beaker and 10 mL of prepared turmeric extract was added to it. The resulting solution was heated at 80°C with continuously stirred by a magnetic stirrer for two hours. Then the final solution was kept undisturbed for two days and brownish crystals of zirconia nanoparticles were obtained.

Synthesis of epoxy resin/ZrO₂ nanocomposites [Bulk adhesives]

First of all, 35 mL of pure epoxy and hardener were mixed in plastic propylene mold. For this, the mixed content was pre-cured for 12 hours at 70°C and post-cured for 12 hours at 120°C. Then, epoxy/ZrO₂ nanocomposites were prepared with different wt.-% (i.e 1, 3, 5 and 10 wt.-%) of zirconia. The various wt.-% of zirconia nanofiller was mixed with 35 mL of epoxy resin and hardener 25 min with continuous stirred with a magnetic stirrer. A similar curing process was followed to the epoxy/ZrO₂ nanocomposite as Then the solutions were pre-cured at 70°C for 12 hrs and post-cured at 120°C for 12 hrs.

c. Characterization

The synthesized ZrO₂ nanoparticles and EP/ZrO₂ nanocomposites were then analyzed to understand their properties and behavior. The characterizations of the prepared samples were applied by powder X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Average particle size was determined from the XRD pattern by calculating the value of full width at half maxima (FWHM) of peak after removing instrumental broadening using Debye-Scherrer formula [18].

$$\text{Average crystalline size } (D) = \frac{0.9\lambda}{\beta \cos\theta}$$

where λ is the wavelength of X-ray, β is full width at half maximum (FWHM) of the most intense XRD peak expressed in radians and θ is Bragg's diffraction angle.

The crystalline structure of ZrO₂ nanoparticles was confirmed from XRD peaks [18]. The experiment was carried out using Rigaku ultima IV model XRD diffractometer employing CuK α radiation ($\lambda = 0.15406$ nm).

FTIR is an analytical technique used to identify organic, polymeric, and in some cases inorganic materials. The FTIR analysis uses infrared light to scan test samples and observe chemical properties [19]. The characterization of synthesized nanoparticle and nanocomposites were done using FTIR analysis and the instrument used for characterization was IR-Prestige-21 (Shimadzu) within the range of 500 cm^{-1} to 5000 cm^{-1} .

d. Compressive strength test

Compressive strength is the resistance of a material to breaking under compression which is the capacity of a material to withstand loads tending to reduce size. Compressive strength is an important aspect in the design of materials or structures and is a vital aspect in determining the load-carrying capacity of the structures [20]. A compressive strength test is a mechanical test measuring the amount of compressive load, a material can bear before fracturing. Normally it is determined by the casting and testing of material specimens in the laboratory. The compressive strengths of various nanocomposites were measured using a universal compression testing machine in the laboratory [21].

Results and Discussion

Size and phase analysis using XRD pattern

The phase purity and crystalline nature of the synthesized zirconia nanoparticle samples were analyzed using XRD diffraction. The diffraction pattern of synthesized zirconia nanoparticles is shown in Figure 1(a). The peaks were obtained at a 2θ value of 28.2 (101), 40.55 (110), 50.66 (202), 59.36 (313), 66.65 (222) which are indexed to tetragonal ZrO_2 phase compared to JCPDS card number 081-1544 [10]. The size of the nanoparticles was calculated via the data obtained from Lorentzian fitting spectra of the corresponding samples given in Figure 1(b).

With the help of Lorentzian fitting and FWHM calculation using the Debye-Scherrer equation, the particle size was calculated to be 35 nm .

Therefore, the synthesized zirconia nanoparticle was successfully characterized using XRD diffraction which indicated that the prepared ZrO_2 nanoparticles were tetragonal phase structures having an average size of 35 nm .

Structural analysis of zirconia nanoparticles using FTIR spectra

The FTIR spectra of the synthesized zirconia nanoparticles which were prepared using the green

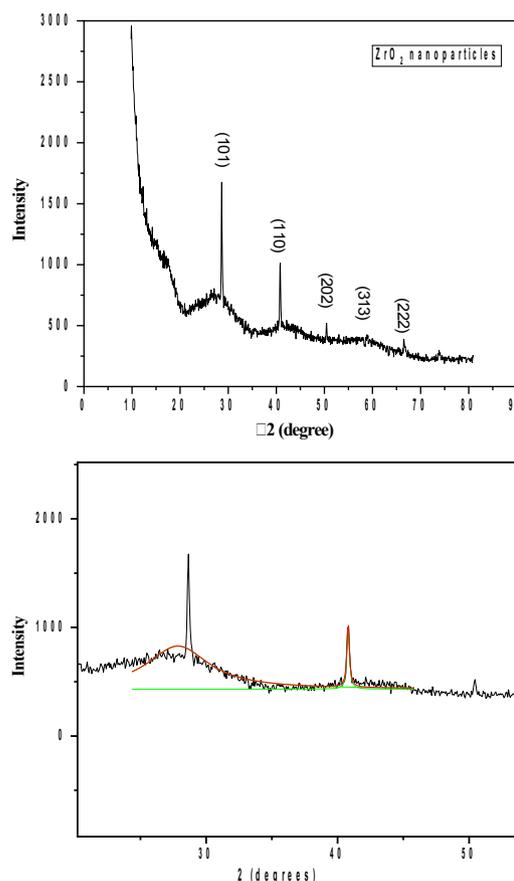


Figure 1: (a) XRD pattern of ZrO_2 nanoparticle synthesized from $0.1\text{M ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and (b) corresponding Lorentzian fitting

synthetic method using $0.1\text{ M ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and *Curcuma longa* extract within the range of 500 cm^{-1} to 5000 cm^{-1} is shown in Figure 2. Thus prepared zirconia nanoparticle using $0.1\text{M ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and *Curcuma longa* extract had broad absorption peak particularly at about 774 cm^{-1} and about 499 cm^{-1} , corresponding to $\text{Zr-O}_2\text{-Zr}$ asymmetric and Zr-O stretching modes respectively, which confirms the formation of ZrO_2 phases based on the works of literature, according to which the respective absorption band are 740 cm^{-1} and 500 cm^{-1} respectively [22].

The significant peaks representing the functional groups present in ZrO_2 are further shown in Table 1. Thus the FTIR spectra confirm that the zirconia was successfully synthesized which indicates from the peaks at 499 cm^{-1} and 774 cm^{-1} and other functional groups from the *Curcuma longa* extract.

Functional group analysis of epoxy resin (EP)/ ZrO_2 nanocomposites

The FTIR spectra of epoxy resin (EP)/ ZrO_2 nanocomposites prepared by mixing the various filler

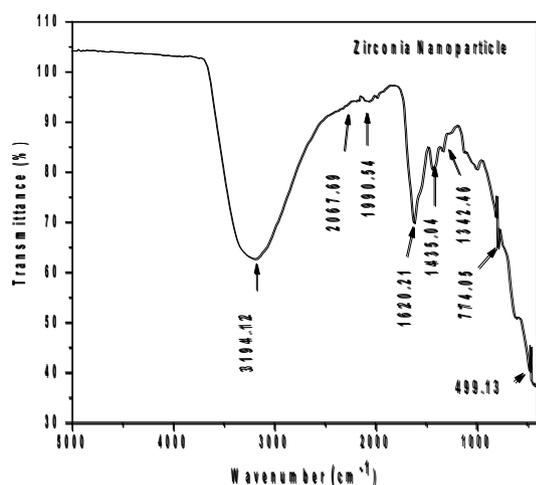


Figure 2: FTIR Spectra of zirconia nanoparticle prepared using 0.1 M $ZrOCl_2 \cdot 8H_2O$ and *Curcuma longa*

Table 1: Functional groups present in zirconia nanoparticles

| Wavelength (cm ⁻¹) | Group | Compounds class |
|--------------------------------|------------------|-------------------|
| 3194.12 | O-H stretching | alcohol |
| 2067.69 | N=C=S stretching | isothiocyanate |
| 1620.21 | C=C stretching | conjugated alkene |
| 1435.04 | C-H bending | alkane |

contents of zirconia nanoparticles and epoxy resin/hardener were analyzed by FTIR Spectroscopy. The FTIR spectra of various nanocomposites were then comparatively studied. The comparative analysis of EP/ZrO₂ nanocomposites is shown in Figure 3.

The comparative study of nanoparticles shows the

absence of a broad absorption band at around 764 cm⁻¹ and about 499 cm⁻¹ referring to the absence of Zr-O₂-Zr asymmetric and Zr-O stretching modes and absence of ZrO₂ phases in the pure epoxy composite. Whereas in the study of epoxy resin (EP)/ZrO₂ (1wt.-%) nanocomposite and epoxy resin (EP)/ZrO₂ (5wt.-%) nanocomposite, the broad absorption band is seen at 763 cm⁻¹-455 cm⁻¹ and 771 cm⁻¹-455 cm⁻¹ respectively. Thus the presence of the ZrO₂ phase is confirmed [22]. The various functional groups present within the nanocomposites prepared using various amount in wt.-% of ZrO₂ nanoparticles and epoxy resin is shown in Table 2.

The FTIR spectra show that the epoxy resin and zirconia nanoparticles were almost mixed up with each other which were indicated by the peak presence in the corresponding wavelength.

Measurement of compressive strength

Compressive strength test or mechanical test measures the maximum amount of compressive load a material can bear before fracturing. The prepared zirconia nanoparticles of different amounts were mixed with epoxy resins and hardeners. Thus prepared composite was compressed between the platens of the compression testing machine having a factor of 3.7 by a gradually applied load. The obtained data measured by universal compression testing machine (UCT) is represented in Table 3. The dimensions of the various nanocomposites' bulk were more or less similar.

The compressive strength of the nanoparticles

Table 2: Significant peak representing functional groups present in the Epoxy resin and its nanocomposites

| Wavelength (cm ⁻¹) | | | Group | Compound class |
|--------------------------------|--|--|-----------------|--------------------------|
| Pure EP | EP/ZrO ₂ Nanocomposite (1% ZrO ₂) | EP/ZrO ₂ Nanocomposite (5% ZrO ₂) | | |
| 3371.57 | 3379.29 | 3356.14 | N-N stretching | Primary amine |
| 2970.38 | 2962.66 | 2962.66 | N-H stretching | Amine salt |
| 2870.08 | 2870.08 | 2870.08 | C-H stretching | Alkane |
| - | 1782.13 | - | C=O stretching | Conjugate acid anhydride |
| 1604.77 | 1604.77 | 1604.77 | C=C stretching | Conjugated alkene |
| 1512.19 | 1504.48 | 1504.48 | N-O stretching | Nitro compound |
| 1458.18 | 1411.89 | - | O-H bending | Carboxylic acid |
| 1373.32 | 1357.89 | 1381.03 | O-H bending | Phenol |
| 1242.16 | 1234.44 | 1234.44 | C-N stretching | Amine |
| 1050.29 | 1033.85 | 1026.33 | S=O stretching | Sulfoxide |
| 825.53 | 825.53 | 825.53 | C=C bending | Alkene |
| 662.00 | 555.50 | 555.50 | C-Cl stretching | Halo compound |

Table 3: Compressibility strength of Pure EP and EP/ZrO₂ nanocomposite

| Cubes | | Pure EP | 1% ZrO ₂ | 3% ZrO ₂ | 5% ZrO ₂ | 10% ZrO ₂ |
|---|---------|---------|---------------------|---------------------|---------------------|----------------------|
| Dimension (cm) | Length | 21.78 | 20.57 | 20.58 | 20.78 | 20.74 |
| | Breadth | 21.44 | 20.18 | 21.50 | 22.12 | 21.10 |
| | Height | 16.93 | 21.13 | 21.44 | 22.56 | 20.00 |
| Weight (g) | | 8.88 | 9.66 | 9.89 | 10.76 | 9.84 |
| Breaking load (g) | | 408 | 510 | 530 | 540 | 515 |
| Compressibility strength (g/cm ²) | | 1509.6 | 1887 | 1961 | 1998 | 1905.5 |

increases on increasing the EP and ZrO₂ nanoparticles ratio as shown in Figure 4. This shows that epoxy resin/zirconia nanocomposites have higher compressive strength than pure epoxy. It means that a significant improvement has been achieved after the addition of Zirconia nanoparticles to epoxy resin. Such results are due to the aggregation of zirconia nanoparticles.

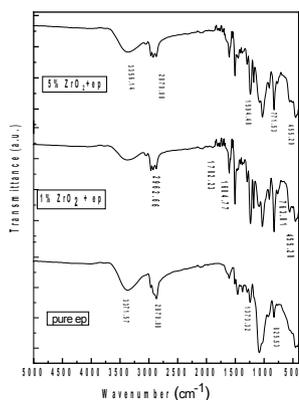


Figure 3: FTIR spectra of pure EP and EP/ZrO₂ nanocomposites (1% and 5% by wt. of zirconia nanoparticles)

The compressive strength of nanoparticles increased up to Zirconia nanoparticles in epoxy nanocomposite and then decreased beyond that. This may be because of the effect of agglomeration of a higher percentage of nanoparticles on the crosslinking of the epoxy resin. A similar result was also recorded in the extraction and characterization of chitosan and preparation of

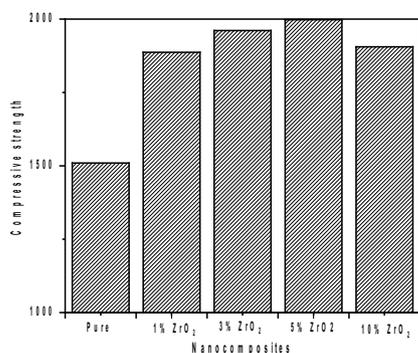


Figure 4: Bar diagram of compressive strength of pure EP and EP/ZrO₂ nanocomposites of different wt.-% of zirconia

nanocomposite with resorcinol formaldehyde resin [23]. The reasons for such deviation can be known by the detailed study of nanocomposites. The internal morphology must be studied *via* TEM. Hence for further information TEM must be done. Overall, the compressive strength of EP/ZrO₂ nanocomposites improved after adding zirconia nanoparticles at any weight fraction.

Conclusion

The implementation of a novel greener approach for the biogenic synthesis of zirconium dioxide nanoparticles using *Curcuma longa* has been successfully carried out. The synthesis method is faster, economical, greener, non-toxic since this method avoids multiple reaction steps, conventional energy sources, and harmful chemicals. FTIR spectra indicated that zirconia nanoparticles and their nanocomposites with epoxy resin were successfully synthesized. The XRD pattern clearly showed that synthesized zirconia nanoparticles were tetragonal structure and the size of the nanoparticle was found to average 35 nm. The FTIR spectra of nanocomposites showed the presence of various compounds. Compression tests on the nanocomposites bulk adhesives indicated that the addition of zirconia nanoparticles to epoxy resin bulk increased the compressive strength. However, the higher amount (about 10%) of zirconia nanoparticles could not favor increasing the compressive strength in epoxy resin/ZrO₂ nanocomposite.

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