SYNTHESIS AND CHARACTERIZATION OF SILVER NANOPARTICLES WITH EPOXY RESIN COMPOSITES

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Silver nanoparticles have excellent, electrical and optical properties that make them ideal for optical, biomedical and antimicrobial applications. The main objective of the current study was to change the surface resistance which may increase its absorption. In this research work silver nanoparticles were prepared by co-precipitation method. For this AgNO₃ and epoxy resin were mixed in 250 ml deionized water and stirred for half hour. Then Ammonia solution NH₄OH was added drop by drop to maintain the PH of solution at (10-11). After filtering the solution the filtrate was dried into oven for 2 hour at the temperature of 150°C. After grinding it was placed into furnace at 1000°C for the time span of 5 hours. Three samples were prepared by increasing the concentration of epoxy (0.25g, 0.5g and 0.75g) in the 0.5g of silver. Crystalline structure was examined by using XRD with peak intensity increase of 320 (a.u) at the angle of 27° . The increase in the peak intensity shows that there is deposition of epoxy resin and the texture has been created in same directions. The sample having 0.5 g epoxy and 0.5g Ag examined by FTIR showed sharp peak at 796.72 cm⁻¹ having C-H bending. Also a broad peak appeared 564.88cm⁻¹ which matches to methyl group. Another sample having 0.75g epoxy in 0.5 g silver examined by FTIR showed a sharp peak at 875.79cm⁻¹ which shows C=C bonding. Three broad peaks were obtained at 1424.36cm⁻¹, 564.88cm⁻¹ and 464.80cm⁻¹ which are due to OH- bonding. The UV-Visible spectroscopy of the sample of epoxy with silver showed that λ_{max} is obtained at 381.98 nm, showing the strong photon absorption of the molecules. It was concluded that epoxy resin composite in silver is a promising approach to enhance the technological applications of silver nanoparticles.

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1. Introduction

Nanotechnology is the engineering of functional systems at the molecular scale. This covers both current work and concepts that are more advanced. Modern synthetic chemistry has reached the point where it is possible to prepare small molecules to almost any structure. These methods are used today to manufacture a wide variety of useful chemicals such as pharmaceuticals or commercial polymers. This ability raises the question of extending this kind of control to the next-larger level, seeking methods to assemble these single molecules into supramolecular assemblies consisting of many molecules arranged in a well-defined manner.

Nanocomposite materials such as those consisted metal nanoparticle dispersed in a polymer matrix which show significant absorbing properties such as chemical and novel physical properties. The epoxy nano composites were used in many field like lead-free interconnecting materials and microelectronic packaging for applications inside the fixed capacitors Over the last eras silver nanoparticles have initiated applications in catalysis, optics, electronics and other areas due to their distinctive size-dependent optical, electrical and magnetic properties. Understanding the reasons of change of the size, shape, surface, and collection state of the silver nanoparticles after addition into a target application is critical for enhancing presentation (Meng et al., 2011). The

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metal nanowires for example silver nanowires (AgNWs) were employed as a conductive fillers. The AgNWS have high thermal conductivity and very small electrical resistivity respectively. These residues of organic molecules on the surfaces of NW are harmful such as they decrease electrical resistivity. Therefore, their application in the Field of electronic packaging is incomplete (Wang at el., 2016).

The most important classes of thermosetting polymers are epoxy resins. Due to their special thermal and mechanical characteristics such as low creep high tensile strength high modulus moisture resistance and thermal stability, epoxy resins have been largely used as high performance adhesive composite materials. Epoxy resins are shiny materials that have very high energies.

In the present study we will synthesize the silver nanoparticles by the co-precipitation technique while its composite with epoxy resin will be formed by solid state reaction method. We will observe the effect of Epoxy resin on Silver nanoparticles. Material founded on the size of metals gives an important key to meet future and present industrial demand in many fields such as Plasmon absorption. It was found that influence of dispersed Ag nanoparticle on the dielectric properties of Ag composite layer. The most use of epoxy resin is polymers in manufacturing industry. Epoxy has glycidyl collections that can be healed to a shape of usable materials. Solvent resistance as well as good balance in thermal, good mechanical properties and chemical, moisture by using epoxy resin. The epoxy is used in coating, structural adhesives, highperformance composite materials manufacture materials, and surface laminates. Epoxy is also normally applied in the field electronic packaging. Conducting adhesives in electronic packing is the shape of epoxy is more operational. (Mohd et al., 2011). Epoxy resins are widely used in protective coatings, adhesives, sealant, fiber reinforced composites and electronic industry due to their outstanding surface properties like low shrinkage, ease of cure and possessing good moisture, solvent and chemical resistance, and excellent adhesion performances (Ren, et al., 2007).

Epoxy resins are used in the manufacture of adhesives, plastics, paints, coatings, primers and sealers, flooring and other products and materials that are used in building and construction applications. Epoxies are thermoset plastics made by the reaction of two or more industrial chemical compounds. The conductive epoxy resin and electrical used for the assembly of electronic devices from digital to microwave applications at many substrates are silver particles filled. To get conductive and high electrical epoxy resin such that Micrometric silver flakes are dispersed into polymer matrix at very high filler concentrations with the combination of poor mechanical properties. The intrinsic electrical and thermal conductivities at the same order than metallic nano as related to silver flakes, carbon nanotubes are well known to show very low percolation thresholds inside epoxy matrix. In this study reviews show that the increasing interest of hybrid filler for electrically conductive and thermally epoxy resin. This type of filler combines with the thermal conductivities and very high electrical of both carbon nanotubes and silver flakes (Marcq et al., 2011). The epoxy resins show special chemical features for example deficiency of byproducts. During curing reactions, the control of degree of cross-linking, low shrinkage up on curing and curing through a wide temperature range between the thermoses set substance. The properties of cured epoxy resins will diverge that depending on the curing conditions and chemical construction of the curing element. Epoxy resins are useful such that good impact resistance, excellent chemical, heat resistance, high electrical insulation and hardness (Ellis 1993). For dielectric measurement of nanoparticles in epoxy resin for example homogeneous material is made. Dielectric size is temperately sensitive to inhomgenities. Epoxy resins are synthesis with good performances for example toughness, high thermal stability rigidity and chemical resistance. In future they are commonly used such as matrix resin for composites. But it is a brittle nature highly cured resin cannot be absorbing energy due to stress. The most common method are used to increasing the toughness of the epoxy resins is to integrate a second phase of dispersed rubbery particles inside the cross linked polymers (Deng, Zhou et al. 2013). Epoxy resins are mostly used in sealant, coatis, fiber reinforced composites and electronic industry because their outstanding surface properties for example chemical resistance, low shrinkage, ease of cure and possessing good moisture, and solvent (Ren et al., 2007). The thermal conductivity of the Ag epoxy composites was improved likened with the epoxy composites and pure epoxy resin.

Wang et al. (2017) studied about silver Nano particles and graphene oxide reinforced with carbon fibre. He used the method of electrophoretic deposition and electrochemical deposition. He also proved that there was an increased in tensile strength and in shear strength. To study about the reinforced composite he used the modern techniques such as FTIR, TEM, SEM, XPS, DCA and AFM and Raman spectrometer. After this he notified that there was an amount of silver Nano particles and also the surface energy roughness of surface was increased significantly. The tensile strength was increased by percentage was about 86.1 % and 36.8 %. The silver Nano particles fill the cracks of epoxy resin and CFs. The epoxy resin and CFs are interlocked and the wettability is also increased of Go sheets. The GO sheets and silver Nano particles improved the interface of epoxy and also increased the metal properties. Pattanaik (2016) evaluated that for high voltage applications epoxy resin were widely used as an insulating material. To increase its mechanical properties ceramic fillers were also subjected to the polymer matrix. In the present research, they found that fly ash was subjected to four different weight percentages. To develop polymer composite to measure its frequency, tests were carried out. By using pulse electroacoustic, the space charge behaviours were also observed.

Xing et al. (2014) evaluated that using electrochemical impedance and absorption of water measurement, coating properties of new epoxy resin ferrite nanoparticles has been achieved. By using X-ray diffraction analysis scanning electron microscopy thermo gravimetric analysis, new materials were achieved. The result indicated that, within epoxy matrix the Nano crystalline indicated a high compatibility and good distribution.

The aim of this research work was to study the structural and morphological effect of different concentrations of epoxy resins on silver nanoparticels, synthesized by co-precipitation technique.

2. Materials and methods

Different methods are used for synthesis of nanoparticles and nanomaterial like coprecipitation, thermal decomposition, micro emulsion, biological and also hydrothermal method. However the co-precipitation method is cost effective that offers simple and control the size of distribution as well as size of particle. It is well known environment-friendly method. In order to synthesize silver nanoparticles, co-precipitation technique was used. This method was comparatively cost effective as far as the mandatory chemical are concerned. This method is very simple inexpensive and less energy consuming. Although the synthesis proceed at comparatively low temperature and long-time is essential until the reaction is completed. The method is shown in block diagram below.



Fig. 1. Co-precipitation method.

We synthesized silver nanoparticles by using co-precipitation technique. All flasks, beakers, burette were washed with deionized water before starting the experiment. The entire chemicals that were used have purity more than 99%.



Fig. 2. Co-precipitation method for synthesis of silver nano particles.

All the chemicals were taken in the stoichiometric ratio. The chemical $AgNo_3$ was dissolved in 250 ml of deionized water and stirred for $\frac{1}{2}$ hour. Then we have added ammonia solution drop by drop so that the PH of 10-11 was achieved. Then we let the solution by putting it in a water bath for an hour. After an hour, we filtered it with the help of filter paper. The filtrate was dried in an oven for about two hours at the temperature of 150 °C.

After grinding, it was placed in a furnace at 1000°C for 5 hours. After five hours, the sintered powder was mixed well with epoxy resin having different weight percentage by solid state reaction method. The nanoparticles with Epoxy resin composite were formed by solid state reaction method. To find the effect of different concentrations of Epoxy resin on the structural and morphological properties of silver, the characterization was done. The different properties were studied by using the X-ray diffraction technique, Fourier transform infra-red spectroscopy and UV-Visible spectroscopy. We have prepared four samples of silver nanoparticles with different concentration of Epoxy resin. We labelled them as AE1, AE2 AE3 and AE4. In sample AE1, silver was 0.5 g and no epoxy resin was added to it. In sample AE2, 0.5 g of silver and 0.25 g of epoxy resin was added. In sample AE3, 0.5 g of silver and 0.5 g of epoxy resin was added. Whereas in sample AE4, 0.5 g silver and 0.75 g epoxy resin was added, as given in Table 1. In all samples silver concentration was same while epoxy resin was varied to study the effect of epoxy resin on silver nanoparticles.

3. Results and discussion

3.1. XRD analysis of sample AE₁ of silver (0.5 g) without epoxy resin

To study the crystalline structure of silver nitrate, XRD was done. When epoxy is 0.0g and Ag is 0.5g than XRD pattern is shown in Fig. 3.



Fig. 3. XRD analysis of sample AE_1 .

It shows the XRD pattern for silver nano particles. The pattern clearly shows that main peaks at (2θ) at 30, 34, 36 and 55 respectively are (111), (200) and (311). Epoxy and silver is found to possess an FCC structure. In untreated sample the peak intensity is 220 (au) at the angle of 220°. The Average crystalline behaviour of silver nano particle was observed by using the Scherer equation.

3.2. XRD analysis of sample AE₂ of silver (0.5 g) with epoxy resin (0.25 g)

To increase the strength of silver material, we added some amount of epoxy resin. The ratio of silver to epoxy in grams was about 0.5:0.25. After preparing sample we used XRD technique to know the crystal structure, physical properties and how epoxy changes the material as shown in Fig. 4.



Fig. 4. XRD analysis of sample AE₂.

It was noted by comparing it with un-tread sample .There will be increase in the peak intensity. We compared it with untreated sample AE1. In the sample AE2 the peak intensity increase, which is 320 (a.u) at the angle of 27°.The increase in peak shows that there will be deposition of epoxy material and there will be texture created in same direction.

3.3. XRD analysis of sample AE₃ of silver (0.5 g) with epoxy resin (0.5 g)

Another sample named as AE3 was prepared by mixing the epoxy in silver with the ratio 0.50g: 0.25 g. We determined the changes that were appeared in the structure of newly prepared sample as shown in Fig. 5.



Fig. 5. XRD analysis of sample AE₃.

From XRD graph it was noted that the peak intensity is sharply increased about 470(a.u) at scattering angle of 260°. The sample AE3 shows increase in peak intensity as compared to samples AE1 and AE2. The increase in intensity shows that the positions of atoms were changed or the dimensions of unit cell were changed.

3.4. XRD analysis of sample AE₄ of silver (0.5 g) with epoxy resin (0.75 g)

The sample of silver by mixing with epoxy was prepared. In sample AE4, 0.75 g epoxy was mixed with 0.5 g silver. The Intensity increases as the number of scatters per unit area for given atomic plane. From the Fig. 6 it is noted that intensity value is 480(a.u) for the angle of 25^{0} as shown in Fig. 6.



Fig. 6. XRD analysis of sample AE₄.

3.5. Comparison of XRD analysis of samples of silver with and without epoxy resin

A comparison was done for the XRD patterns of all samples of silver with and without epoxy resin as shown in Fig. 7.



Fig. 7. Comparison of XRD analysis of samples of silver with and without epoxy resin.

It was noted that when the amount of epoxy in silver was increased, more intense peak is obtained which shows that there will be change in the position of atoms. More intense peak shows that there will be deposition of epoxy material in silver. More intense peak is obtain in sample AE4 having more epoxy in that sample. The intense peak shows that there will be more texture in sample AE4 because of large amount of epoxy. Results showed that the strength of material gradually increases by adding the epoxy in silver material.

3.6. FT-IR analysis of sample AE₁ of silver (0.5 g) without epoxy resin

To study the molecular composition and structure of the specimen, Fourier transform infrared spectroscopy is used. In this technique infrared light of various wavelengths is used. In Fourier transform infrared spectroscopy the light falls on the sample and many of the molecules absorbs the light in the infra-red region. By the value of wave number we determine that what type of functional group is present in the material. In this technique we measure absorbance of infrared radiations by prepared sample versus wavelengths. We prepared three samples of silver with epoxy resin. The first sample of silver nitrate is untreated and the other two samples were prepared by mixing the epoxy resin of 0.5g and 0.75g in 0.5g silver respectively. The results of FTIR are shown below in Table 1.

Serial no	Transmittance (%)	Wave number cm ⁻¹
1	95	3790.87
2	96	3000
3	97	2366.54
4	98	1441.87
5	99	877.24
6	100	576.34

Table 1. FT-IR analysis of silver without epoxy resin.

The characterization of first untreated sample of silver nitrate without epoxy was done by FTIR is shown in the Fig. 8. The graph is between transmittance (%) and wave number (cm^{-1}) .



Fig. 8. FT-IR analysis of silver without epoxy resin.

There are the two regions in the graph. The first region is functional group region which lies (4000-1600 cm⁻¹) and the other region is finger print region which lies (1600-400cm⁻¹). From the graph a small peak is obtained at 3000cm⁻¹ and 3016.70cm⁻¹ in the functional group region. By relating it to the reference table it is noted that these values corresponds to alkene group having O-H stretching having intermolecular bonded. While in finger print region a broad peak is obtained at 1441.87cm⁻¹. The broad peak is due to H-bonding. A sharp peak is obtained at 877.24cm⁻¹ having C-H bending.

3.7. FT-IR analysis of sample AE₃ of silver (0.5 g) with epoxy resin (0.5 g)

Another sample AE3 was prepared by mixing 0.50 g silver with 0.5g epoxy resin. The characterization was done by FTIR. The transmittance and wave number are shown in Table 2.

Serial no	Transmittance (%)	Wave number(cm ⁻¹)
1	96.0	3016.65
2	96.5	2366.15
3	97.0	1424.93
4	97.5	876.08
5	98.0	562.14
6	98.5	465.33

Table 2. FT-IR analysis of silver (0.5 g) with epoxy resin (0.5 g).



Fig. 9. FT-IR analysis of silver (0.5 g) with epoxy resin (0.5 g).

The results in Fig. 9 showed that small peaks appeared at 3016.65cm⁻¹ and 2366.15 cm⁻¹ in the functional group region. These values showed that this material belongs to OH- stretching

group. In the finger print region a sharp peak is obtained at 796.72 cm-1 having C-H bending. Also a broad peak appears 564.88cm-1 which matches to methyl group.

3.8. FT-IR analysis of sample AE₄ of silver (0.5 g) with epoxy resin (0.75 g)

Another sample AE4 was prepared by mixing 0.50 g silver with 0.75g epoxy resin. The characterization was done by FTIR. The transmittance and wave number are shown in Table 3.

wave number(cm)
3016.70
1424.36
875.79
504.88
464.80

Table 3. FT-IR analysis of silver (0.5 g) with epoxy resin (0.75 g).

FT-IR	analysis c	of sample AE4	of 0.5 g silver	with 0.75 g epoxy	y resin is showi	n in Fig. 10	0
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Fig. 10. FT-IR analysis of silver (0.5 g) with epoxy resin (0.75 g).

The sample was prepared by mixing epoxy and silver in ratio 0.75 g: 0.5 g respectively. The characterization of this sample is shown in the figure. In the functional group region a broad peak is obtained at 3016.70cm-1 which belongs to alkene. In the finger print region a sharp peak is appeared at 875.79cm-1 which shows C=C bonding. Also three broad peaks are obtained at 1424.36cm⁻¹, 564.88cm-1 464.80cm-1 which are due to OH- bonding.

3.9. UV-Visible analysis of sample of silver with epoxy resin

We have found the surface plasmon resonance of silver mixed with epoxy resin by UV-Visible spectrophotometer. The absorbance at different wavelengths is shown in Table 4.

Table 4. UV-Visible analysis of sample of 0.5 g silver with 0.75 g epoxy resin.

Serial no	Absorbance	wavelength(nm)
1	0.83	327.55
2	0.94	381.98
3	0.68	506.22

To test the how much energy is absorbed by the sample prepared by mixing epoxy and silver. The spectrum of uv- vis spectroscopy is showen in the Fig. 11.



Fig. 11. UV-Visible analysis of sample of silver with epoxy resin.

It was noted that λ_{max} is obtained at 381.98 nm. At this λ_{max} the molecules have strong photon absorption. It also tells how many incoming radiations absorbs by the substance which is under examimation. The molcules absorbs the light of wavelength 381.98 nm which lies in in the visible region having pale yellow color. At this wavelength absorbance is increased due to increase of epoxy concentration because absorbance is directly proportional to the concentration of the absorbing sample.

4. Conclusions

In this study, silver nanoparticles were produced using co-precipitation method. The incorporation of nanoparticles into epoxy resins offers environmentally benign solutions to enhancing the integrity and durability of coatings, since the fine particles dispersed in coatings can fill cavities. The usefulness of nanoparticles brings many advantages and opportunities to paint and coating industry. A comparison was for the XRD patterns of all samples of silver with and without epoxy resin showed that when the amount of epoxy in silver was increased, more intense peak is obtained showing the increase in the metallic properties of silver. It showed that there will be change in the position of atoms. More intense peak obtained in the sample AE4 (0.5 g silver,0.75 g epoxy) showed that there will be deposition of epoxy material on silver. There will be more texture in sample AE4 because of large amount of epoxy. Results showed that the strength of material gradually increases by adding the epoxy in silver material. Further study can be possible on the fact that epoxy coatings containing nanoparticles offer significant barrier properties for corrosion protection and reduce the trend for the coating to blister or delaminate.

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