Preparation, characterization and electrical study of gum arabic/ZnO nanocomposites

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Abstract. Gum arabic (GA)-mediated chemical synthesis was carried out for obtaining ZnO nanoparticles (ZnO-NPs) (particle size of ZnO $\approx$ 40 nm) which, in turn, was used for preparing ZnO–biopolymer nanocomposites. The dielectric study of this synthesized products is reported in this paper. The synthesized products were characterized by X-ray diffraction, Fourier transform infrared, and transmission electron microscopy for their structure and morphology study. The frequency dependence of dielectric constant and dielectric loss of these GA–ZnO nanocomposites were analysed in the frequency range of 100 Hz–5 kHz. In addition, the dielectric property of these nanocomposites (0–15 wt% filler concentration) was analysed with respect to frequency in the temperature range 30–80°C. A high dielectric constant of 275 is achieved for the sample with 10 wt% of ZnO filler. The dielectric property of GA–ZnO nanocomposites is attributed to the interfacial and orientation polarization.

Keywords. Polymers; chemical synthesis; infrared spectroscopy; dielectric properties.

1. Introduction

Gum arabic (GA) is an inexpensive, hydrophilic, non-toxic, biocompatible and totally biodegradable polymer.^{1–3} It is a weak polyelectrolyte that carries charged groups (carboxylate and amine groups), negatively charged above pH 2.2.⁴ When adsorbed on a particle surface, it creates steric hindrance, bridging or charge-patch depending on the pH of the particle solution.⁵ It is being widely used for industrial purposes in the food industry, and to a lesser extent in textiles, ceramics, lithography, cosmetic and pharmaceutical industry.⁶ The GA molecule can act as a reducer, bridging agent, template, stabilizing agent for oxide and metal nanoparticles.^{5,7–10} Polymer nanocomposites with high dielectric constant are always desirable for transducers, piezo-sensors, hydrophones in producing electromagnetic antennas, etc. Use of inorganic filler ZnO shows some interesting microscopic, spectroscopic, thermal, mechanical, electrical, especially dielectric and conductive properties.^{11–16} Semiconducting ZnO nanoparticles (ZnO-NPs) have some unique properties like large exciton binding energy ($\sim$ 60 meV) and large direct bandgap of 3.3 eV at room temperature.^{17,18} These properties of ZnO provide higher breakdown voltages and sustain large electric fields and offer low electric noise.¹⁹ By choosing particular kind of matrix and filler nanoparticles, one can modify the desired properties of the nanocomposite for a particular application. As reported in literature, ZnO nanocomposites were investigated for electrical

study using the matrix of polystyrene, polyaniline, ethylene vinyl acetate, polyvinylidene fluoride, polyvinyl alcohol, starch-based polymer, epoxy resins, polyurethane, acrylic, etc.^{11–14,20–27} There are several reports in the literature on the dielectric studies of ZnO-doped nanocomposites with polymers, e.g., acrylic/ZnO,¹¹ polyurethane/ZnO,¹² epoxy resin/ZnO,²⁰ polyvinylidene-fluoride–ZnO,^{21,22} polyaniline (PANI)–ZnO,²⁵ polyvinyl alcohol/ZnO.^{26,27} Hence, the incorporation of the ZnO-NPs in the biopolymer GA matrix was explored with the hope that it may lead to some new and interesting results as compared to other reported matrices as biopolymers have not been explored in this context.

In this work, ZnO-NPs were successfully prepared using GA as stabilizing agent and then GA/ZnO nanocomposite and investigated dielectric properties over a low frequency range of 0.1–5 kHz and temperature range of 30–80°C. The bio-polymeric nanocomposites, consisting of ZnO nanoparticles as fillers in various proportions, were characterized using electric modulus. ZnO nanoparticles were prepared with thermal decomposition of zinc hydroxide embedded in a GA matrix. Nano-filler contents have a large surface area as compared to micro-fillers, and there is a vast growing field to investigate nano-filler interaction with polymer matrices for basic understanding of the filler effect due to nanostructure.¹⁶

2. Experimental

2.1 Preparation of ZnO-NPs

The synthesis of ZnO-NPs in the solution of GA (mol. wt. = 250,000) biopolymer was conducted at room temperature. To

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prepare a solution (A), zinc nitrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] was dissolved in distilled water under vigorous stirring at room temperature. To prepare another solution (B), GA in distilled water was prepared under vigorous stirring at room temperature. Solutions A and B were mixed and NH_4OH solution was added to it dropwise. pH factor of the final solution was maintained at constant value of 12. The white precipitate was filtered and washed with distilled water for several times. Then the precipitates were dried in oven at 90–100°C for several hours and the yield was about 90%. To reduce the agglomeration among the smaller particles, the GA molecule containing many –OH functional groups was used in this synthesis method. These functional groups help to bind to surface of nanoparticles at the initial nucleation stage. Finally, the dried product was subjected to heat treatment at temperature 600°C in air for 2 h to remove residues of GA polymer.

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ammonium hydroxide [NH_4OH], GA and ethanol used were all analytical grade. All of the chemicals were used as-received without any further treatment.

2.2 Preparation of GA/ZnO nanocomposites

The GA/ZnO nanocomposites were prepared by adding appropriate amount of ZnO-NPs to the GA solution under sonication at ~60°C with sonication frequency of 33 kHz. The details of the sample composition, temperature and drying method are given in table 1. Note that the solution mixing of each component under sonication was applied to overcome the agglomeration of the nanoparticles in GA water solution.

2.3 Characterization

The structure of the nanocomposites was investigated with Philips X-ray diffractometer (Model PW 1710) with filtered Cu-K_α radiation of wavelength $\lambda = 0.1541874 \text{ nm}$. The microstructure of the specimens was observed under transmission electron microscope (TEM, Philips, Model-CM12). Fourier transmission infrared (FT-IR) spectra of GA/ZnO films, coated on dry potassium bromide (KBr) pellet, were recorded on FT-IR 8400S spectrometer with resolution setting of 4 cm^{-1} and range of 400–4000 cm^{-1} . Each sample was scanned 4 times. The fine powders of GA–ZnO

nanocomposites were isostatically pressed into pellets under pressure of 5 bar for 5 min. The capacitance of the sample was measured by using a LCR meter (Model-LCR HiTESTER-3532-50, Hioki) in 100 Hz–1 MHz frequency range and in 30–80°C temperature range. Thermal stability of the nanocomposites within the working temperature range has been checked and confirmed by using a thermogravimetry analyzer (STA 449F3 Jupiter, Netzsch, Germany).

3. Results and discussion

3.1 Microstructure of ZnO with X-ray diffraction (XRD)

The powder XRD patterns of the samples, obtained at room temperature are shown in figure 1. XRD peaks of ZnO powder can be indexed with hexagonal structure: $\text{P}_{63\text{mc}}$ and all the diffraction peaks are in agreement with JCPDS data (Card no. 00-079-2205, $a = 3.250 \text{ \AA}$, $c = 5.207 \text{ \AA}$). The results show that ZnO-NPs consist of pure phase and no characteristic peaks for other impurity like $\text{Zn}(\text{OH})_2$ appear. The average crystallite size D is calculated using the Scherrer formula ($D = 0.93\lambda/\beta \cos \theta$), where λ is the characteristic wavelength of Cu-K_α ($1.541874 \text{ \AA}$), β the full-width of diffraction line at half the maximum intensity and θ the Bragg angle. The value of D is found to be $36 \pm 2 \text{ nm}$.

3.2 Morphology of ZnO-NPs

To confirm the particle size of the ZnO-NPs, the samples were investigated through bright field image by the TEM. A typical TEM image and selected area electron diffraction (SAED) pattern of the as-prepared ZnO nanostructure are given in figures 2 and 3, respectively. From the micrographs, the average particle diameter was calculated to be ~40 nm. The results extracted from TEM reasonably agree with those obtained from XRD taking into consideration that the TEM image gives the size of the individual particles, whereas the size calculated from the XRD patterns represents average size. SAED patterns were taken from the specimens. The estimated d values observed from the SAED patterns are in good agreement with those estimated from the XRD data.

3.3 FT-IR characterization of GA/ZnO nanocomposites

The structure–bonding and interactions of the biopolymer nanocomposites have been elucidated in the FT-IR analysis as presented in figure 4. The interaction between ZnO-NPs and GA matrix is studied by analysing the differences in C–O region and N–H region of FT-IR spectra. The GA molecule and ZnO-NPs mainly interact through the surface hydroxyl groups of the ZnO-NPs. The major and strongest vibrational modes in the GA spectrum are those located at 1075, 1420, 1626, 2365, 2925 cm^{-1} and a broad absorption band is at 3000–3600 cm^{-1} . In all the biopolymer–ZnO samples, FT-IR

Table 1. Sample composition and temperature of the GA/ZnO nanocomposites.

Sample	Composition	Sonication temperature, time and drying method
S00	Gum arabic (GA)	Sonication
S05	1 g GA + 50 mg ZnO	temperature—60°C,
S10	1 g GA + 100 mg ZnO	time—1 h;
S15	1 g GA + 150 mg ZnO	drying method—oven
S100	Zinc oxide	dried at 90–100°C

Figure 1. Powder XRD pattern of ZnO nanoparticles.

Figure 2. Typical TEM image of ZnO nanoparticles.

Figure 3. Typical SAED image of ZnO nanoparticles.

band peaks at 420, 423 and 464 cm^{-1} indicate the characteristics of ZnO.¹⁵ The presence of ZnO in the polymer matrix can be confirmed by the peak observed around 558 cm^{-1} in the PVA/ZnO composites due to Zn–O stretching, which is not observed in the polymer.²⁸

The strong vibrational mode between 3000 and 3600 cm^{-1} is assigned to the stretching vibrations of the O–H bond and the other vibrational mode at 1626 cm^{-1} is assigned to the stretching vibrations of the C=O bond of carboxylate group.²⁹ Relatively low intense modes at 1068 and 1429 cm^{-1} are due to the stretching vibrations of the C–O bond, and the weak mode at 2924 cm^{-1} is originated from

the stretching vibrations of the C–H bond.^{29,30} The ZnO-NP composites possess absorption bands between 2960 and 2850 cm^{-1} due to stretching vibrations of the C–H bond, and 1470 and 1350 cm^{-1} due to scissoring and bending of the C–H bond. The strong peak at 1599 cm^{-1} is originated from carboxylate group of the GA molecule.³¹ The FT-IR spectrum of GA shows a weak absorption band at 1420 cm^{-1} , which is assigned to COO[−] symmetric stretching.³⁰ The predominant peaks at 1730 and 1240 cm^{-1} confirm the acetyl content of GA. The strong band at 1200–900 cm^{-1} is originated from carbohydrate's content, various vibrations of C–O–C glycosidic and C–O–H bonds.^{15,32}

Figure 4. FT-IR spectra of GA/ZnO nanocomposites: S00, S100, S05, S10 and S15.

Figure 5. Variation of dielectric constant with temperature for different GA/ZnO nanocomposite samples at 2 kHz frequency.

Based on the above FT-IR analysis, the spectrum between 1000 and 1150 cm^{-1} originates from the crosslink characteristic region of the composite.³³ In the spectrum, pure GA gives the broad peak and ZnO gives a prominent peak but at slightly shifted position, whereas that of the nanocomposites shows a lower intensity peak which seems to be composite of two. Due to the large surface area of nanoparticles, the -OH group in nanocomposites has much more significant effects on the crosslink density.³³

3.4 Dielectric constant

Variation of dielectric constant as a function of temperature for various weight percentages of ZnO-NPs in GA is as shown in figure 5. The permittivity (ϵ^*) as a function of frequency is described by the complex permittivity

$$\epsilon^*(\omega) = \epsilon'(\omega) - j\epsilon''(\omega),$$

where the real part $\epsilon'(\omega)$ and imaginary part $\epsilon''(\omega)$ are the components for the energy storage and energy loss, respectively, in each cycle of electric field. The dielectric constant (ϵ_r) was calculated using the following equation: $\epsilon_r = Cd/\epsilon_0 A$, ϵ_0 , d , A and C being the permittivity in vacuum ($8.854 \times 10^{-12} \text{ C}^2\text{N}^{-1}\text{m}^{-2}$), thickness, area and the measured value of sample capacitance, respectively. The dielectric loss [$\epsilon''(\omega)$] is described as follows:

$$\epsilon''(\omega) = \epsilon'(\omega) \cdot \tan \delta. \quad (1)$$

Electric modulus is defined as the inverse quantity of complex permittivity by the equation

$$\begin{aligned} M^*(\omega) &= \frac{1}{\epsilon^*(\omega)} = \frac{1}{\epsilon'(\omega) - j\epsilon''(\omega)} = \frac{\epsilon'(\omega)}{[\epsilon'(\omega)]^2 + [\epsilon''(\omega)]^2} \\ &\quad + j \frac{\epsilon''(\omega)}{[\epsilon'(\omega)]^2 + [\epsilon''(\omega)]^2}, \\ &= M'(\omega) + jM''(\omega), \end{aligned}$$

where $\epsilon'(\omega)$, $M'(\omega)$ are the real and $\epsilon''(\omega)$, $M''(\omega)$ the imaginary parts of permittivity and electric modulus, respectively.

Dispersion of dielectric constant over frequency was observed in the low frequency region. There is a significant effect of ZnO on ϵ_r value of nanocomposites at lower frequency region. It has been observed that the dielectric data are independent of the sample thickness and this observation suggests that in nanocomposite samples the dielectric properties are not due to the electrode polarization or surface barrier at the electrode.^{34,35} Electrical relaxation effects in the polymer matrix composites arise mainly due to interfacial effects, phase transitions and polarization or conductivity mechanisms and interfaces with varying geometrical characteristics.^{36,37} The effective dielectric constant of polymer/filler composite material depends on the dielectric constants of the polymer and the filler, size and shape of the filler and the volume fraction of the filler, the dielectric constant of the interphase region, volume of the interphase region and on the type of coupling agents.³⁸⁻⁴⁰ The dielectric constant of the polymer nanocomposites shows a remarkable increase when a semiconducting nanoparticles are incorporated as a filler, and this behaviour can be attributed to the conductivity increase of semiconducting fillers with temperature and interface polarization interaction.⁴¹⁻⁴³ Earlier works demonstrated the dielectric behaviour of ZnO nanocomposites with various polymer systems and table 2 is a compilation of the reported dielectric constant (ϵ_r) values from the literature for ZnO/polymer composites. A comparison of the presently observed dielectric constant values with the reported ones shows clearly that ZnO/GA nanocomposite provides the highest value of dielectric constant.

The interfacial polarization in polymer nanocomposites with structural inhomogeneity can be identified by low-frequency ($\sim 100 \text{ Hz}$ – 100 kHz) dielectric measurement based on Maxwell–Wagner–Sillars's polarization⁴⁴ because of the accumulation of mobile charges at the interfaces of the composite. Figure 6 shows the variation of dielectric constant of GA/ZnO nanocomposite S10 with frequency. The dielectric constant, as shown in figure 6, decreases

Table 2. Compilation of the dielectric constant (ϵ_r) values for ZnO/polymer composites available in the literature.

Nanocomposites	Synthesis method	Dielectric constant (ϵ_r)	Remark	Reference
Acrylic/ZnO	Solution mixing	~ 3 –4 in the range of 1–600 MHz	ϵ_r increases with the ZnO (3.75 nm) incorporation	11
Polyurethane/ZnO	<i>In-situ</i> suspension polymerization	~ 5 –7 in the range of 10 kHz–1 MHz	ϵ_r increases with the ZnO (59 nm) incorporation	12
Epoxy resin/ZnO	Solution mixing	~ 5 –7 in the range of 1 kHz–1 MHz	ϵ_r decreases with the ZnO (30 nm) incorporation	20
Polyvinylidene-fluoride–ZnO	Solution mixing	~ 2 –12 at 1 kHz varying temperature 300–550 K	ϵ_r increases with the ZnO (<100 nm) incorporation	21,22
Polyaniline (PANI)–ZnO	Solution mixing	~ 5 –45 in the range of 1 kHz–1 MHz	ϵ_r decreases with the ZnO (5–9 nm) filling in insulating form of PANI	25
Polyvinyl alcohol/ZnO	Solution mixing (ultrasonic)	~ 10 –40 in the range of 100 Hz–2.5 kHz	ϵ_r increases with the ZnO (~ 40 –60 nm) incorporation	26,27
Gum arabic/ZnO	Solution mixing	~ 50 –250 at 2 kHz varying temperature 300–350 K	ϵ_r increases with the ZnO (< 40 nm) incorporation and maximum with 10% ZnO filler	The present work

Figure 6. Variation of dielectric constant of GA/ZnO nanocomposite S10 with frequency. **Figure 7.** Variation of dielectric loss with frequency of different GA/ZnO nanocomposite samples at 70°C.

with the increase in frequency. This may be attributed to the tendency of dipoles in polymeric samples to orient themselves in the direction of the applied field. At higher frequency the dielectric constant remains almost constant, as it is difficult for the dipoles to rotate at high frequency range.

The variation of dielectric loss with different frequencies for different weight percentages of ZnO in GA at 70°C temperature is shown in figure 7. Figure 8 shows the variation

of dielectric loss with frequency for the sample S10 at different temperatures and figure 9 shows the variation of the dielectric loss for all samples with temperature at frequency of 2 kHz. Dielectric losses are of mainly four kinds: distortional, dipolar, interfacial and conduction loss. Among these, two important losses are the distortional and interfacial losses—distortional loss is the effect of electronic and ionic polarization mechanisms; interfacial loss originates from the polarized interface induced by the fillers.^{45,46}

Figure 8. Variation of dielectric loss of the GA/ZnO nanocomposite sample S10 with frequency at different temperatures.

Figure 9. Temperature variation of the dielectric loss for all GA/ZnO nanocomposite samples at 2 kHz frequency.

Experiments have clearly demonstrated that the polymer surface interactions can lead to properties for the polymer layer, which are, in general, different from that of the bulk polymeric material.⁴⁶ The energy dissipated in a dielectric material is proportional to the dielectric loss tangent. Therefore, a low dielectric loss is preferred to reduce the energy dissipation and signal losses, particularly for high frequency applications. Generally, a dissipation factor under 0.1% is considered to be quite low and 5% is high.⁴⁷ A very low dissipation factor is desired for RF applications to avoid signal losses, but much higher values can be tolerated for energy storage applications such as decoupling.⁴⁸ The measured dielectric loss is the contribution of two phenomena—the dipolar orientation and interfacial polarization of surface charges between the electrode and GA/ZnO nanocomposite surface.

Figure 10. Variation of real M' of the electrical modulus with frequency for the GA/ZnO nanocomposite sample S10 at different temperatures.

Electric modulus is defined as the inverse quantity of the complex permittivity. To interpret electrical relaxation effect, electric modulus formalism offers some advantages over other treatments as a large variation of dielectric constant and dielectric loss at low frequencies and high temperature. In this method, one can easily neglect the errors arising due to electrode nature, the electrode–specimen contact, the injection of space charges, and absorbed impurities.³⁷ The enhanced values in the low frequency range indicate the co-existence of electrode polarization and interfacial relaxation phenomena. Existence of electrode polarization can be neglected for the studied samples for the reasons stated above. Separating the contribution of each effect is not an easy task by measuring only dielectric constant and thus the electric modulus formalism will be employed for the interpretation of dielectric data. In polymer nanocomposites, electrical relaxation phenomenon occurs from both the polymer matrix and the filler. With the presence of the filler, interfacial phenomenon [Maxwell–Wagner–Sillars (MWS effect)] is expected to occur.⁴⁴

The variation of real M' and imaginary M'' parts of the electrical modulus as a function of frequency and temperature are shown in figures 10 and 11, respectively, for sample S10. At the low temperature and above 70°C, it does not reach the origin due to dielectric relaxation process or existing electrode polarization.⁴⁹ The increase in the values of M' and the subsequent development of M'' peaks with the increase in frequency is a characteristic behaviour of a dielectric dispersion. In the low frequency range, the small increase of M' values with the temperature increase results from the restriction of the motion of large parts of molecular chains in the polymer. Orientation of the large dipoles at the interfaces becomes harder and permittivity is increased with the consequent increase in M' values.

From figure 10 (for the sample S10), it is obvious that at lower frequencies M' values are very small, and tend to be zero indicating the removal of electrode polarization.^{50,51}

Figure 11. Variation of real M'' of the electrical modulus with frequency for the GA/ZnO nanocomposite sample S10 at different temperatures.

Figure 12. Cole-Cole plots of the GA/ZnO nanocomposite S10 sample for different temperatures.

Figure 13. Cole-Cole plots for GA/ZnO nanocomposite samples S05, S10 and S15 at 70°C.

However, when M' increases with the increase in frequency, it may be attributed to the relaxation processes at higher frequencies.⁵² With increasing temperature the value of M' reduces due to increase in mobility of the polymer segment and charge carriers, i.e., the orientation of the charge carriers and molecular dipoles becomes easier at high temperatures.

As shown in figure 12, both M' and M'' increase with the increase in temperature until 70°C due to increase in resistivity for ZnO nanoparticles. However, M' and M'' decrease with increasing temperature above 70°C which can be attributed to the glass transition in GA. The polymer cannot create enough resistance for the ionic motions. Figure 13 shows the variation of M' and M'' for three samples S05, S10 and S15. The electric modulus slightly decreases with the increase in ZnO nanoparticle content due to the effect of interface between the GA matrix and ZnO nanoparticle. When ZnO nanoparticle volume increases, the quantity of the matrix decreases and consequently the conductivity effect decreases. The change of M' and M'' with change in the nanoparticle content of the nanocomposite can be explained due to an increase in relaxation time with heterogeneity.⁵³

4. Conclusion

In this work, the variation of dielectric constant and the dielectric loss of GA/ZnO nanocomposites, combined at different mass ratios, with temperature and frequency were found to be nonlinear experimentally. A high dielectric constant was found for the sample with 10 wt% of ZnO filler. The effect of ZnO on dielectric constant value of nanocomposites was found to be more pronounced at lower frequency region. The dielectric properties of ZnO-NPs are attributed to the interfacial and orientation polarization. The synthesized composites exhibit a low dielectric loss at higher frequency region, which is preferred to reduce the energy dissipation and signal losses, particularly for high frequency applications.

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