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Research Article

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Abstract

Herein we present the synthesis of K2ZrO3 by solution combustion method and in situ coating technique is used for the coating of poly (ortho-anisidine) (POA) on prepared nanoparticles. Furthermore, a series of Gelatin/poly-o-anisidine coated K2ZrO3 polymer nanocomposite were fabricated by varying the POA coated K2ZrO3 viz 0, 1, 2, and 4 wt % using the solvent intercalation method. High-resolution transition electron microscopy (HRTEM) was used to study the size and morphology of the synthesized nanoparticles and polymer coated nanoparticles. From the results it is cleared that the average size of the prepared nanoparticles and polymer coated nanoparticles are around 18-20 and 95-100 nm respectively, and the polymer coated nanoparticles are spherical in shape, and form a core shell. The phase purity and microcrystalline behavior of the prepared nano particles, POA coated nanoparticles and gelatin nanocomposites were analyzed by using X-ray diffraction (XRD). From the results it was noticed the changes in the peak intensities of nanocomposites films, and a little shift in the peak position towards the lower 2θ values. Scanning electron microscope [SEM] and energy dispersive spectroscopy[EDX] were employed for the analysis of the surface morphology and the elemental composition of the prepared nanoparticles and nanocomposites. Fourier transform infrared spectroscopy was used to assess the physical interactions between the components in nanocomposites. The thermal stability and effect of polymer coated nanoparticles inclusions on glass transitions temperatures were studied by using Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) respectively. UV–Visible spectroscopy technique is used to study the optical properties of the Gelatin/POA@K2ZrO3 nanocomposites and the optical constants of nanocomposites were determined. From the results it is clear that, with increase in POA coated K2ZrO3 nanoparticles concentration from 0 to 4 wt % in a gelatin matrix, the band gap energy (Eg) value drops from 4.13 to 2.16 eV, and the refractive index rises from 1.529 to 3.25.

1 Introduction

Biodegradable nanocomposites are next-generation materials that use biopolymer-based materials to ease the waste disposal problem to greater extent. Some of the potential renewable polymers include carbohydrate (starch, cellulose), protein (wheat gluten, soy protein, and gelatin), and com-derived plastics such as polylactic acid (PLA) [1, 2]. Gelatin is one of the natural polymers (a denatured fibrous protein), and its polarity corresponds to the numerous amino acids in its structure, which improves its capacity to interact with polar polymers and different fillers. Gelatin can be used in a variety of biological and pharmacological applications [3, 4]. The applications of gelatin were limited due to its low electrical, mechanical, and water stability. However, when compared to petroleum-based plastics, biopolymers have poor electrical, mechanical, and water vapour barrier qualities. Owing to this many researches has been conducted to discover strategies to improve the qualities of biopolymers, such as chemical modification, blending with other biopolymers to produce intermediate properties, and the inclusion of a plasticizer to reduce brittleness [5, 6].

Polymeric nanocomposites containing inorganic nanoparticles as a filler have recently emerged as a promising approach to overcome the performance limitations of pure polymeric materials. Furthermore, particular physicochemical features, metal oxides are the most commonly used nanoparticles [7]. Metal oxide nanoparticles have been hybridized with multi-elements such as CsAlO2, SrZrO3, and La2CuO4 to improve their characteristics [8–10]. Metal-doped zirconium oxide nanoparticles as shown to be an excellent proton conductor with good thermal and chemical stability, a good contender for a solid-state electrolyte in fuel cells, and a
possible material for humidity sensor applications in this regard [11, 12]. Padma et al. [13] revealed that barium zirconate (BaZrO$_3$) nanoparticles with an average particle size of 40 nm and a high dielectric constant may be successfully manufactured using a combustion technique. Song et al. have also looked into Y-doped Na$_2$ZrO$_3$ as a high-capacity cathode for sodium-ion batteries [14].

Furthermore, a few possibilities on metal oxide (like ZnO) sites, including Li, Na, and K, operate as deep acceptors, contributing to p-type conductivity. They are suitable for optoelectronic devices, light-emitting diodes, photodetectors, sensors, solar cells, optical switches, photocatalysis, waveguides, and piezoelectric materials because of their properties [15, 16]. One method of designing nanocomposites with low bandgap energy, greater refractive index, and UV shielding uses is to include nanoparticles into polymeric matrices [17, 18]. A thorough review of the literature reveals that several recent studies have focused on the characteristics of gelatin-based biopolymer nanocomposites integrated with various nanoparticles such as ZnO, CdS, and CuO$_2$ [19–21].

Conducting polymers such as poly (diphenylamine), polyaniline, and polypyrrole [22-23] as well as their composites with inorganic particles such as SiO$_2$ [24]. In addition to recent research on graphene oxide, TiO$_2$ [25] has been extensively explored [26-28]. Electrorheological (ER) materials with a core-shell structure have also been reported, with better ER effects such as thermal stability, electro-response and dispersibility [28]. It is very useful to use spherical silica as a core material to produce core-shell structured functional hybrid particles, especially with conducting polymers as a shell.

The synthesis of core-shell particles is simple and easy since silica surfaces can be easily functionalized and the particles have a spherical configuration. As a result, silica-based core-shell structured particles have been widely used in different materials. The silica core, for example, has been utilized with a variety of metallic shells (Au, Ni, and Ag) [29]. Polymers in general (PMMA, PS) [30, 31] and conducting polymers (polypyrrole, PEDOT) [32, 33]. Similarly, as a derivative of polyaniline, poly (o-anisidine) (POA) is a promising conducting polymer (PANI). In this investigation, POA was used as an optical characteristic. The ortho-position of o-anisidine has a methoxy group (-OCH$_3$), unlike aniline. When o-anisidine is polymerized, the methoxy group creates a steric effect that inhibits the mobility of electric charge carriers along the polymer backbone. This functional group inhibits interactions between polymeric chains by increasing inter-chain distance. Furthermore, POA's reactivity is known to be higher than that of PANI, implying that POA has a higher oxidative polymerization yield [34, 35]. The hollow POA microsphere has been reported as a way to the particle sedimentation constraint [36]. POA has been employed as a sensor, a membrane electrode, and an electrochemical super capacitor as a result of these properties [37-39]. Despite this research homogeneous POA coating on potassium zirconate surfaces is difficult. This study's aim is the synthesis of K$_2$ZrO$_3$ particles coated uniformly with POA was synthesized using a simple method.

Through literature review on the effects of K$_2$ZrO$_3$ nanoparticles on modified thermal stability, glass transition temperature and optical band gap energy of gelatin nanocomposites are restricted, and no results found on gelatin/ POA@ K$_2$ZrO$_3$ nanocomposites. Owing to this, the present research work aim to synthesize and characterize gelatin/ POA@ K$_2$ZrO$_3$ as low-cost, biologically safe, and environmentally acceptable biopolymer nanocomposites.

2 Materials And Methods
2.1 Materials

O-anisidine (99% purity) and Gelatin are purchased from (Type B, Sigma-Aldrich USA) Propylene Carbonate (PC) ($C_4H_6O_3$), Potassium nitrate, Chloroform, Hydrochloric acid (HCl), Ammonium persulphate, Zirconium (IV) nitrate pentahydrate (AR grade SD Fine Chemical), ($Zr(NO_3)_2.5H_2O$) are used as an oxidant, Glycine ($C_2H_5N_2O$) as fuel. Sodium dodecyl sulphate is used as a surfactant to reduce the size of polymer particles. Double distilled water is used as solvent to prepare gelatin nanocomposites, Deionized water also used in this process.

2.2 Synthesis of poly (O-anisidine) (POA)

The chemical oxidative polymerization technique is used for the synthesis of POA by using o-anisidine as a monomer. 5.8 gm of o-anisidine added to 10 ml benzene mixed well and dissolved in 30ml of 1.5M HCl aqueous solution and cooled to 0 and 4°C. Later, the solution of 14.5 gm of Ammonium persulphate (APS) in 30 ml of 1.5M HCl was added slowly to the above o-anisidine solution followed by stirring for 24hr. After stirring a dark green precipitate of the polymer was obtained, filtered, and washed using deionized water and methanol to remove the oligomers and other radicals. The obtained POA polymer was dried in an oven at 100°C for 6 hr to get in solid powder state [40].

2.3 Synthesis of poly (o-anisidine)/$K_2ZrO_3$

The POA coated $K_2ZrO_3$ nanocomposites was prepared by in situ polymerizations of o-anisidine. 0.5% $K_2ZrO_3$ (0.00876gm) and 3% o-anisidine (0.0526gm) monomer was added to 30 ml of 1.5 M HCl solution and stirred for 1h. Then 0.175gm of sodium lauryl sulphate was added slowly drop wise to the suspension mixture in 20 ml of $H_2O$ and 20 ml of chloroform, allowing the solution to be stirring for 12 hr at room temperature. The product was collected by filtering and washing the precipitation with methanol and deionized water and dried at 60°C for 24hr [41-42].

2.4 Fabrication of blend Gelatin /Poly (O-anisidine)/$K_2ZrO_3$ by hybrid nanocomposites

Solvent intercalation technique was used to fabricate gelatin hybrid nanocomposites with different concentrations of POA@$K_2ZrO_3$ nanoparticles, viz, 0, 1, 2, and 4 wt %. Required amount of gelatin solution was prepared by dissolving 12 g of gelatin in 200 ml of double-distilled water at 80°C and 2ml of plasticizer (Propylene Carbonate) was added followed by ultrasonication for 30 min. The homogeneous solution was poured into a glass mold which was previously cleaned and the solvent was allowed for slow evaporation at room temperature to get hybrid nanocomposites. The thickness of the obtained hybrid nanocomposites ranges from 0.18 mm and 0.19 mm ± 0.02mm [43, 44].

2.5 Experimental Technique

The size, surface morphology, and compositional characteristics of the as-obtained POA@$K_2ZrO_3$/Gelatin hybrid nanocomposites were evaluated by using a transition electron microscope (TEM) (JEOL/JEM 2100, Japan). The microstructure parameters of pristine POA@$K_2ZrO_3$ nanoparticles and their gelatin hybrid nanocomposites were evaluated by X-ray diffraction (XRD) (Proto, AXRD table top, Canada) with Cu-Kα radiation source ($\lambda=1.54$ Å) worked at 30 kV and 20 mA at a scan speed of 0.05°/sec in the 2θ ranging from 10°- 80°. The morphological properties of fabricated hybrid nanocomposites were documented by using the scanning electron microscope
The Fourier transform infrared (FTIR) spectroscopy (JASCO 4100 spectrometer Japan) was employed to study the physical and chemical interaction between components of nanocomposites. The optical properties and optical constants of the fabricated gelatin hybrid nanocomposites were evaluated by using UV-visible spectroscopy (Shimadzu 1800, Japan) from the wavelength ranging from 200-1100 nm. Contact angle meter (HO: IADCM-081, India) was used to measure the contact angle and surface energy.

3 Results And Discussion

3.1 Structural studies

The XRD pattern of K$_2$ZrO$_3$ nanoparticles, POA, and POA@K$_2$ZrO$_3$ nanocomposites are shown in Fig. 1(a) The distinct diffraction peaks of K$_2$ZrO$_3$ nanoparticles were seen at 2$\theta$ centered 30.1°, 35.1°, 50.3°, 59.9°, and 62.8° corresponding to d-spacing 0.296, 0.255, 0.178, 0.154, and 0.147 nm and Miller indices of 101, 111, 201, 211 and 202, respectively [46]. The sharp peak of the obtained K$_2$ZrO$_3$ nanoparticles is owing to the crystalline nature. The Debye-Scherrer formula is used to compute the crystal size/Scherrer length (L) of K$_2$ZrO$_3$ nanoparticles [44]

$$L = \frac{0.9\lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

where $\beta$ is the full width at half maximum (FWHM) of the peak, CuK=0.15406 nm is the wavelength, and $\theta$ is the Bragg diffraction angle K$_2$ZrO$_3$ nanoparticles have an average crystallite size (L) of 20 nm± 0.5, and K$_2$ZrO$_3$ has a monoclinic crystal structure. Furthermore, in pristine POA structure fig. 1a, there are two crystalline segments. The lower degree of organization of the crystalline section can be seen as the broad and low-intensity peak at 2$\theta$=17.9° (hkl 101), while the higher-order portion of POA can be seen in the partially intense peak at 25.6° (hkl 200), which is attributed for the semi-crystalline nature of the polymer [47]. In the core shell POA@K$_2$ZrO$_3$ some new extra crystalline peaks have been observed along with shift of the peak. This change in the position of the peaks can be attributed to the interaction between the POA and nanoparticles.

The XRD profile of the K$_2$ZrO$_3$ nanoparticles centered in the 2$\theta$ values of 30.10, 35.10, 50.30, 59.90, 62.80° and the POA coated nanoparticles 23.81, 26.46, 30.66, 32.85, and 36.31°, which clearly shows that nanoparticles and POA are in good physical interaction. The XRD patterns of pristine gelatin and its hybrid nanocomposites with 0, 1, 2, and 4 wt% POA@K$_2$ZrO$_3$ are shown in Fig. 1b. The XRD profile shows that gelatin has a diffraction peak centered at 2$\theta$=20.5° (hkl 101), indicating the amorphous nature. From the X-ray profile, it was clear that the peak centered at 20.5 was still flattened and broad, which can be attributed to the significant changes in the diameter of gelatin's triple helix with increasing in POA@K$_2$ZrO$_3$ content in nanocomposites, owing to the good physical interaction between POA@K$_2$ZrO$_3$ and gelatin. The presence of a core shell POA@K$_2$ZrO$_3$ prevents gelatin from re-crystallizing and the intensity of the peak at 2$\theta$=17.9° is strongly influenced by the presence of POA@K$_2$ZrO$_3$ in the gelatin matrix. Due to partial aggregation of nanoparticles, the gelatin/4wt% of POA@K$_2$ZrO$_3$ nanocomposites shows a slight increase in crystallinity [48]. X-ray pattern of the gelatin/POA@K$_2$ZrO$_3$ composites shows the peaks in the 2$\theta$ ranges from 29.3 to 30.5 which has the characteristic peak of nanoparticles. Furthermore, there is a slight change in the position of the 2$\theta$ when
compared to the x-ray profile of the nanoparticles alone, which can be attributed to the interaction between the gelatin and the nanoparticles.

3.2 Fourier Transform Infrared (FTIR) analysis

FTIR spectra of gelatin/POA@K$_2$ZrO$_3$ nanocomposites in the wave number range 400-4000 cm$^{-1}$ are given in Fig. 2a and 2b. The interactions between distinct constitutions in the nanocomposites are shown by FTIR spectral data. The vibration peaks of pure gelatin are 3313 and 2820 cm$^{-1}$, due to the =OH and –NH group and the –CH$_3$ of the aromatic ring respectively. After increasing by 4% POA@K$_2$ZrO$_3$, the absorption band at 1768 cm$^{-1}$ due to the C=O group in gelatin is shifted to a lower frequency by approximately 10 cm$^{-1}$, which could be attributed to the formation of H-bonds between the –NH group in POA and the C=O bunches in gelatin structure [47]. The emergence of another wide peak 3330-3250 cm$^{-1}$ with a peak at 3259 cm$^{-1}$ is attributed to the stretching vibration of NH of POA as the dosage of core shell POA@K$_2$ZrO$_3$ in gelatin is increased. Multiple peaks in the spectrum at 1731-1467 cm$^{-1}$ with an exponential peak at 1580 cm$^{-1}$ are due to the quinoid C=C of aromatic rings of POA, which overlaps with the pinnacle of gelatin's C=C ring. Stretching vibrations of the –COO group peak at 1135 cm$^{-1}$. The characteristic peaks of –CH$_3$ bending out of the plane of the benzenoid ring are 867-764 cm$^{-1}$ [43]. The characteristic peaks of the POA@K$_2$ZrO$_3$ composite can be found at 3259, 1889, 1719, 1616, 1445, 1086, 812, 715, 648, and 592 cm$^{-1}$ [49], as shown in Fig. 2 and these peaks are observed to shift to lower wave number in contrast to those blended POA, showing the existence of the POA@K$_2$ZrO$_3$ composite.

POA's core shell and K$_2$ZrO$_3$ nanoparticles have a strong connection in the wave number range 700-500 cm$^{-1}$ the influence of K$_2$ZrO$_3$ nanoparticles can also be seen. Fig. 2b-d reveals IR absorption peaks at 686, 670, 647, 593, and 563 cm$^{-1}$, indicating that metal oxide nanoparticles are present in nanocomposites, which is also confirmed by the presence of the peaks around 562 and 715 which attributed to K-O non-bridging oxygen and the contribution of bridging oxygen for K-O-Zr and K-O-K bonds, which consecutively and these peaks are in a good correlation with information revealed elsewhere.

4 Optical Studies

Fig. 3a shows the optical absorbance of pristine K$_2$ZrO$_3$ nanoparticles and core shell POA@K$_2$ZrO$_3$ from 200-800nm. It can be shown that the intense peak 212.27 nm of K$_2$ZrO$_3$ nanoparticles has red shifted to 201.27 nm for core–shell POA@K$_2$ZrO$_3$ due to physical interactions between nanoparticles and POA (nanoparticles–O: NH-POA). The peak of POA@K$_2$ZrO$_3$ was detected via the chain of aromatic nuclei at 212.27 nm, which corresponds to $\pi\rightarrow\pi^*$ transitions. For core shell nanoparticles, typical bands at 227.01 and 283.14 nm, as well as a wide band in the wavelength ranging from 400-800nm focused at 453nm were observed, which can be attributed to the $\pi\rightarrow\pi^*$ benzenoid rings of the ortho-anisidine ring [49]. The polaronic transition (polaron-$\pi^*$) of protonated POA is responsible for the peak at 283.14 nm. Further broad peaks are attributed around 453.81 nm because of the polaron band transition ($\pi$-polaron) of the POA backbone [50]. In Fig. 3b, the optical response of pure gelatin and its nanocomposites comprising 1, 2, and 4wt% POA@K$_2$ZrO$_3$ has been shifted. The absorption bands at 281nm in the ultraviolet-visible spectra of pure gelatin film are attributed to $n\rightarrow\pi^*$ (of O molecules). The gelatin / POA@K$_2$ZrO$_3$ nanocomposites films had more strong absorption peaks than gelatin, implying that the nanoparticles in the film are distributed uniformly. The intensity of the $\pi\rightarrow\pi^*$ transition peak increased from
312.19 to 368.96 nm in a red shift. The polaron peak at 698.80 nm in nanocomposites films was accompanied by a change in absorption edges from 380.90 to 496.48 nm, indicating that nanocomposites had stronger responsiveness to visible light than gelatin.

Fig. 4a illustrates the dependence of absorbance coefficient on photon energy (h\(\bar{\nu}\)) for gelatin/ POA@K\(_2\)ZrO\(_3\) nanocomposites. It can be clearly noticed that adding 4wt% POA@K\(_2\)ZrO\(_3\) to gelatin host increases its absorption at UV region, especially at higher >3 eV, which corresponds to absorption edges at 340-400 nm and 510-735 nm. As a result of the formation of charge transfer interaction between the components in nanocomposites, a shift in absorption edge toward lower energy was observed. The absorption increase ratio (AIR) of Gelatin/POA@K\(_2\)ZrO\(_3\) nanocomposites at 3.21 eV, can be calculated using eq. 2 as follows [46].

\[
AIR = \frac{(\alpha_{NC} - \alpha_G)}{\alpha_{NC}} \times 100 \%
\]

where \(\alpha_G\) and \(\alpha_{NC}\) are the absorption coefficients of gelatin and its nanocomposites respectively, at maximum absorption. Fig. 4b depicts the calculated data, which is given in Table 2. The results revealed that the core shell of POA@K\(_2\)ZrO\(_3\) improves the 3.2 eV value of pure gelatin, with AIR values increasing from 0 to 70.7% as POA@K\(_2\)ZrO\(_3\) content increases from 0 to 4wt%.

The Tauc's plots were plotted by \((\alpha h\bar{\nu})^2\) versus \(h\bar{\nu}\) in order to measure the direct band gap energy (\(E_g\)), of the nanocomposites, as shown in Fig. 5. For K\(_2\)ZrO\(_3\) nanoparticles, POA, and core shell POA@K\(_2\)ZrO\(_3\) the obtained \(E_g\) values are 4.58, 3.48, and 2.67 eV, respectively. Lower \(E_g\) values of core–shell POA@K\(_2\)ZrO\(_3\) indicate that K\(_2\)ZrO\(_3\) nanoparticles disrupt the normal configuration of the POA network. From the graph, it is clear that the \(E_g\) values of the gelatin doped with POA@K\(_2\)ZrO\(_3\) nanocomposites decreases with increased concentration of the POA@K\(_2\)ZrO\(_3\) ranging from 4.13 eV for pure gelatin and 3.21, 2.83, and 2.16 eV doped with 1, 2, and 4wt% of POA@K\(_2\)ZrO\(_3\) respectively. The large reduction in \(E_g\) is due to new excitation energy levels formed beneath the usual band gap as a result of charge transfer between gelatin and POA@K\(_2\)ZrO\(_3\) core shell which has altered the gelatin structure and therefore reduced \(E_g\).

The refractive index for pure and doped gelatin nanocomposites was plotted as a function of wavelength in Fig. 6a, and the \(n\) values at maximum \(\lambda_{285}\) nm are provided in Table 2. According to the findings, the \(n\) increases dramatically as the amount of POA@K\(_2\)ZrO\(_3\) in gelatin films increases with the optimum value being \(n=3.25\) for gelatin /4wt% POA@K\(_2\)ZrO\(_3\) compared to 1.53 for pure gelatin matrix. Increased polarization fillers created the dipole of polar functional groups (oxygen atoms) in gelatin chains as a result of the presence of (K\(^+\), Zr\(^{4+}\)) with small ionic radius in nanoparticles and polar multi atoms -N- in POA. This leads to an increase in the absorption of incident light; increasing the \(n\) value is useful in various applications of ophthalmic lenses, filters, optical adhesives, anti-reflection coatings, and sophisticated optoelectronic fabrications.

When an electromagnetic wave passes through a material, the extinction coefficient (k) indicates the loss of energy by the material can be computed by using an equation. [51]

\[
k = \frac{\alpha\lambda}{4\pi}
\]
where $\lambda$ is the wavelength of the incident light and $\alpha$ is the absorption coefficient. In the UV region, the value of the extinction coefficient, $K$, decreases with increasing wavelength with a small peak, which is attributed to significant absorption in this region Fig. 6b Since this coefficient of absorption dominates, this behavior is most likely comparable to that of an absorbance spectrum. In the visible region and near-infrared region, $\alpha$ is reduced and $\lambda$ dominates. Therefore, the values of $K$ increase as the wavelength increases, confirming a directly proportional relationship between $K$ and $\lambda$. The $K$ values for 4 wt.% gelatin /POA@K$_2$ZrO$_3$ are the highest, while the $K$ values for pure gelatin are the lowest, due to the absorption of free carriers, the extinction coefficient drops considerably in the ultraviolet region, particularly around 355-410 nm.

5 Thermal Studies

5.1 Differential Scanning Calorimetry (DSC)

In Fig. 7 the DSC thermogram of produced gelatin films doped with various concentrations of POA@K$_2$ZrO$_3$ is shown, and the findings are listed in Table 3. The glass transition temperature ($T_g$) of the gelatin films containing 4wt% POA@K$_2$ZrO$_3$ rose to 96°C, compared to 82°C for the pure gelatin film, as shown in the figure. The inclusion of POA@K$_2$ZrO$_3$ increased the thermal stability of the gelatin film, according to this study. These findings clearly reveal that the temperature of gelatin's phase transition altered as the quantity of POA@K$_2$ZrO$_3$ increased. The formation of extra intermolecular forces, such as hydrogen bonds, in the presence of POA@K$_2$ZrO$_3$ content might explain this tendency. This hypothesis is consistent with a previously published theory of molecular interactions and chain stiffness. The utilisation of edible films as a packing material is intimately tied to their thermal qualities. Heat may cause structural shifts in protein networks by disrupting chemical bond connections, as is well known. The endothermic peak of the pure gelatin film was seen at 82°C, which might be due to the helix coil transition of gelatin and other additives disturbing the order of molecular structure linked to water dissociation and binding.

Thermal stability is usually connected with a high melting temperature ($T_m$), a high $T_m$ value equates to good thermal stability. The lower $T_m$ for the film made with 4 wt% POA@K$_2$ZrO$_3$ was ascribed to the hydrophobic characteristic given into the gelatin molecular structure by the POA@K$_2$ZrO$_3$ addition. This feature aided water evaporation and the reduction of hydrogen bonds. Furthermore, the increase in the number of hydrogen bonds in the gelatin-based film matrix may have contributed to the increased $T_m$. Furthermore, the transition heat rose progressively with increasing POA@K$_2$ZrO$_3$ concentrations, as reported. This pattern might be described in the following way: The POA@K$_2$ZrO$_3$ additive quantity resulted in the construction of a convoluted channel in the film matrix for heat to move through, as well as a more compact structure, which took a lot of energy to degrade gelatin. The polymer network undergoes ordered configuration when the concentration of POA@K$_2$ZrO$_3$ is raised to 0–4 wt% due to an increase in intermolecular forces. Excess POA@K$_2$ZrO$_3$, which has a greater specific surface area, is thought to wrap around gelatin molecules [52].

5.2 Thermal gravimetric analysis (TGA)

Thermogravimetric analysis (TGA) has proved to be a suitable technique to investigate the thermal stability of polymeric systems. From the TGA thermogram it is cleared that the three distinct thermal degradation steps for pure gelatin and POA@K$_2$ZrO$_3$ nanocomposites [53]. The temperature range of decomposition, the percentage
weight-loss, and the ash content values are given in Table 4. The first step weight loss occurred in the temperature range 29.09°C- 225.95 °C and is due to the evaporation of moisture and physisorbed water molecules corresponding to a weight loss in the range of 14.25 %. At the second stage, the thermal degradation occurred in the temperature range 225.95°C - 440.35°C, with a major weight loss of 47.68 % corresponding to the dissociation of intermolecular and intramolecular hydrogen bonding and structural decomposition with the liberation of CO₂, NH₃, HCN, C₂H₄, and CH₄ due to the degradation of the protein [54].

The third stage thermal degradation occurred in the temperature range 440.35°C - 655.96°C was due to the decomposition of carbonaceous matter with a weight loss of 37.13 %. The thermal decomposition of pure gelatin and its POA@K₂ZrO₃ nanocomposites show similar patterns Fig.8. From the table it is clear that the thermal stability of POA@K₂ZrO₃ nanocomposites is higher than that of pure gelatin. This improvement in the thermal stability is due to the presence of nanofiller, which acts as a barrier to maximize the heat insulation and to minimize the permeability of volatile degradation products of the material [55]. The results conclude that the thermal stability of the gelatin has improved with the dispersion of POA@K₂ZrO₃ in the gelatin matrix.

6 Surface Morphology Analysis

6.1 Scanning Electron Microscope and Energy Dispersion X-ray

The SEM photomicrographs was employed to evaluate the nanoparticle's dispersion in the gelatin matrix and to understand the morphology of the composites. However, the SEM image in Fig. 9 showed the semi-spherical shape extended in the cluster agglomeration of particles. Fig. 9(a)-(i) displays the morphology of the pure gelatin and POA@K₂ZrO₃ doped nanocomposites. A fine dispersion of nanoparticles in the gelatin matrix can be observed. The increasing weight percent of POA@K₂ZrO₃ in the gelatin matrix enhances the surface roughness of nanocomposite films, which could be attributed to the strong physical interactions between the nanoparticle and the polymer matrix.

When increasing the concentration level of dopants, the distance between the filler and filler becomes shorter and the agglomeration of nanoparticles can be observed. A nano-needle compound is generated from nanolamellar potassium zirconate, as seen by a scanning electron microscope image [56, 57]. The elemental composition of the prepared nanocomposite was confirmed by employing EDX analysis and the result is presented in fig. 10. From the results it is confirmed that the nanocomposites contains nanoparticles which is coated with POA

6.2 High resolution Transmission Electron Microscopy (HR-TEM) and Selected area electron Diffraction (SAED)

The morphological study of K₂ZrO₃ and POA@K₂ZrO₃ were evaluated by HR-TEM and selected area electron diffraction (SAED) studies. The HR-TEM images in Fig. 11 clearly indicate the core-shell structure of the POA@K₂ZrO₃ particles. TEM photomicrographs of POA@K₂ZrO₃ nanoparticles shows that the nanoparticles are spherical in shape and that the particle size obtained is between 18-20 and 95-100 nm. The thin grey/black covering around the nanoparticles was the POA which forms shell around the K₂ZrO₃ surface. The TEM picture of pure K₂ZrO₃ is shown the POA shell around nanoparticles which is around 5 nm in thickness [58].
7 Wettability Studies

The ability of a liquid to wet the surface of a solid substance is a crucial property that is influenced by the solid surface qualities (hydrophobic or hydrophilic) as well as the liquids utilized. Wetting characteristics of gelatin nanocomposites films doped with 1, 2, and 4% POA @ K₂ZrO₃ were studied by using contact angle and are presented in Fig. 12. The wettability of pure gelatin is shown by its contact angle of 61.61°. As illustrated in Fig. 12, the lower values imply increased surface energy, which provides a strong attractive cohesive force that pulls the water droplet down and causes it to spread out, with the findings listed in table 5. The inclusion of 1, 2, and 4 wt percent POA@K₂ZrO₃ into the gelatin matrix resulted in convex meniscus morphologies of water droplets with 70.52°, 75.69°, and 76.61°, respectively which are in good agreement with the results reported elsewhere [59]. This contact angle finding indicates that gelatin nanocomposites are still wettable, although they are less so than pure gelatin. When compared to pure gelatin, the interfacial tension between nanocomposites and water droplets is lowered. As a result of the higher contact angle, the surface energy and interfacial tension of the nanocomposites are reduced.

8 Conclusion

Using the solvent intercalation technique, a series of Gelatin nanocomposites were successfully synthesized with various concentrations of POA@K₂ZrO₃ nanoparticles, viz 1, 2, and 4wt %. The structural, thermal, morphological, water contact angle and optical properties of the core shell in the gelatin matrix were evaluated. SEM analysis of the nanocomposites confirms that the nanoparticles are uniformly distributed throughout the gelatin matrix without any agglomeration. TEM analysis confirms the coating of the POA on prepared K₂ZrO₃ nanoparticles. The Gelatin-nanocomposites are thermally stable up to 440° C. Following the integration of nanoparticles in gelatin, DSC thermograms reveal an increase in, T_g, and Tm which in turn supports the increase in crystallinity. FTIR spectra show a change in the absorption peaks of –OH groups of gelatin due to physical interaction between POA@K₂ZrO₃ and Gelatin. The opto-electrical characteristics of hybrid K₂ZrO₃ nanoparticles have been thoroughly investigated. It was discovered that the refractive index of nanocomposites is substantially influenced by the content of nanoparticles. The nanocomposites band gap energy drops from 4.13 eV for pure gelatin to 2.16 eV for gelatin/4wt% POA@K₂ZrO₃. The contact angle values of nanocomposite films were higher as compared with pristine gelatin. It indicates a reduction in the wettability of the nanocomposites surfaces and their surface energy is slightly lower than the surface tension of the water. As a result, increasing the POA@K₂ZrO₃ content of gelatin film reduces its hydrophilic nature significantly. The obtained results suggest that gelatin/POA@K₂ZrO₃ nanocomposites were the promising candidates for multiple applications.

References

52. X. Wu, Y. Liu, W. Wang, Y. Han, A. Liu, J Food Process Eng, 40(3), e12469 (2017).

**Tables**

Table 1  The structural components of Gel/ POA@K$_2$ZrO$_3$ nanocomposites.

Table 2 The optical parameter of Gel/ POA@K$_2$ZrO$_3$ nanocomposites.

Table 3  Data obtained from DSC thermogram for Gel/ POA@K$_2$ZrO$_3$ nanocomposites.
<table>
<thead>
<tr>
<th>Gelatin/(POA+K₂ZrO₃) (Wt/Wt %)</th>
<th>2θmax (degree)</th>
<th>FWHM (β)</th>
<th>d spacing (Å)</th>
<th>Scheerer length (L) (Å)</th>
<th>δ 10⁻⁵</th>
<th>Lattice strain 10⁻³</th>
<th>R</th>
<th>SF</th>
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<td>2.961</td>
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<table>
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<tr>
<th>Content of POA@K₂ZrO₃ wt%</th>
<th>A (cm⁻¹)</th>
<th>AIR (%)</th>
<th>E_g (eV)</th>
<th>n(λ₂₈₅)</th>
<th>Extinction co-efficient(10⁻³)</th>
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Table 4  Thermal decomposition of Gelatin/POA@K₂ZrO₃ nanocomposites.

Table 5  The study of the wettability of gelatin/POA@K₂ZrO₃ nanocomposites.
<table>
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<tr>
<th>Gelatin/POA@K₂ZrO₃ (wt/wt%)</th>
<th>steps</th>
<th>Temp range(°C)</th>
<th>T₀</th>
<th>Tₚ</th>
<th>Tₜ</th>
<th>Weight loss (%)</th>
<th>Ash (%)</th>
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<th>Gelatin/(POA+K₂ZO₃)</th>
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<th>Surface Energy</th>
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<td>100/00</td>
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**Figures**

**Figure 1**

XRD profile (a) pristine POA, K₂ZrO₃ and POA@K₂ZrO₃, nanoparticles (b) pure gelatin, gelatin doped with 1, 2 and 4wt% POA@K₂ZrO₃ nanocomposites.
Figure 2

FTIR spectra of (a) K$_2$ZrO$_3$ and POA@K$_2$ZrO$_3$, (b) Gelatin + POA, and 1, 2, 4 wt% POA@K$_2$ZrO$_3$ composites.

Figure 3
Optical absorbance (a) pristine $K_2ZrO_3$ and core-shell POA@$K_2ZrO_3$ (b) pristine Gelatin and 1, 2, and 4wt% Gelatin/ POA@$K_2ZrO_3$.

Figure 4

(a) Absorption coefficient (b) AIR (%) and band gap energy as a function of photon energy for gelatin/ POA@$K_2ZrO_3$ films.
Figure 5

Tacu's plots for direct band gap versus photon energy for gelatin/ POA@K$_2$ZrO$_3$ nanocomposites.
Figure 6

(a) The refractive index (b) Extinction coefficient of pure gelatin and gelatin/POA@K₂ZrO₃ nanocomposites as a function of wavelength.

Figure 7

DSC thermograms of gelatin/ POA@K₂ZrO₃ nanocomposites.
Figure 8

Typical TGA and its derivative thermograms of Gelatin/POA@K$_2$ZrO$_3$ nanocomposites.

Figure 9

Scanning Electron Microscopy (SEM) (a-i).
Figure 10

Energy Dispersion X-ray (EDX).
Figure 11

Transmission Electron Microscopy images and Selected Area Electron Diffraction (SAED) of the prepared nanocore.
Figure 12

Contact angle and the shape of water droplets on the surface of gelatin/POA@K$_2$ZrO$_3$ composites.