

CaTiO₃-Dispersed PVA Nanocomposite Film: Structure, Morphology, Bonding, and Thermal Studies

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ABSTRACT

Fine particles of metal oxides-dispersed polymer nanocomposites develop new properties of polymeric materials and hence various applications. This new class of materials contributes a lot to the field of materials science. The current investigation is reporting the synthesis of calcium titanate (CaTiO₃) nanomaterials by self-propagating combustion reaction using poly(ethylene glycol) (PEG) as a fuel. CaTiO₃-dispersed poly(vinyl alcohol) (PVA) nanocomposite (PVA/CaTiO₃) is prepared by solvent casting method. As prepared, CaTiO₃ and its PVA composite materials are well characterized by various characterization tools such as X-ray diffraction (XRD), scanning electron microscope, and Fourier-transform infrared respectively. Particle morphology and its size are well confirmed by transmission electron microscopy study. The thermal behavior of the prepared PVA composite sample was studied by thermogravimetric analysis.

Key words: Calcium titanate, PEG, Poly(vinyl alcohol), Nanocomposite, Fourier-transform infrared, X-ray diffraction, TEM, Thermogravimetric analysis.

1. INTRODUCTION

Titanium-based bimetallic oxide materials attracted many researchers due to its properties and applications [1,2]. Transition metal-based oxide materials have gained much attention due to their structural arrangements. These materials are considered much for their applicable-oriented properties and its stability at variable particle sizes [3]. The particle size of the materials responses to the development of special properties in the materials. Bimetallic oxides containing titanium metal play a vital role in many areas of science and technology by metal-metal and metal-oxygen bonding. Calcium titanate (CaTiO₃) is titanium-based bimetallic oxide known for its semiconductive, ferroelectric, and photorefractive properties, and hence, is widely used in electronics such as capacitors, oscillators, and filters [4,5]. It has been studied extensively and is also considered an electroceramic material. Further, it is renamed as a microwave ceramic owing to its dielectric response in the microwave spectrum. In addition, the photocatalytic activity and dynamic efficiency of CaTiO₃ have been investigated in decomposing organic dye waste in aquatic environments [6,7]. CaTiO₃ has been developed as an implant material for biomedical applications in composites with hydroxyapatite [8]. Several approaches are adopted for the synthesis of well-phase-formed CaTiO₃ nanomaterials for specialized applications [9,10]. Out of the literature methods, a self-propagating solid-state combustion reaction was found to be very effective and also requires low-cost precursor materials. Polymers may be considered a fuel for the combustion reaction leads phase-formed product.

The fine dispersion of nanoscale bimetallic oxides in polymeric materials constitutes a new class of materials and has received much attention from researchers due to its various applications [11].

Polymer nanocomposite formed by dispersion of CaTiO₃ in the polymer matrix constitutes great importance among classes of nanocomposite materials in terms of applications [12]. Dispersion of nanosized CaTiO₃ in poly(vinyl alcohol) (PVA) forms composite material, shows enhanced thermal stability, and is easy to produce. It also shows good chemical and physical properties which response to broad applications in various fields [13]. The incorporation of ceramic fillers like CaTiO₃ into the PVA matrix has significantly enhanced the ionic conductivity and thermal stability of the pure PVA. Recently, membranes based on PVA have received considerable attention from researchers due to its non-toxicity, good film-forming ability, low cost, good mechanical strength, and chemical stability [14-17]. The incorporation of CaTiO₃ into the polymer matrix of cross-linked PVA has been shown to reduce the crystalline nature of the matrix and improve their performance in a considerable manner [18-20].

The current experimentation is reporting the synthesized CaTiO₃ nanoparticles by combustion route using polymer fuel. The solvent casting method is used in the preparation of PVA nanocomposite (PVA/CaTiO₃).

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2. EXPERIMENTAL

2.1. Materials and Methods

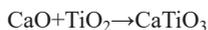
Chemicals used in the present investigation are of Analytical grade (AR grade) and were purchased from Sigma Aldrich. Combustion with polymer fuel method was used for the preparation of the CaTiO_3 sample. The solvent casting method is used for the preparation of PVA/ CaTiO_3 nanocomposite film.

2.2. Synthesis of CaO and Titanium dioxide (TiO_2) Nanoparticles

Calcium chloride is mixed with PEG in the weight ratio 1:5 and grounded well in a pestle and mortar for fine grinding. The resultant solid is transferred into a china dish and heated in an air atmosphere until the carbonaceous flame was completely tuned to a noon sooty flame. Transferred the preheated reaction product into a silica crucible and ignited at 900°C in a muffle furnace. Initially, PEG melted, then frothed, and finally forms a crystalline CaTiO_3 sample. Cooling the product to room temperature gives white-colored oxide residue as CaTiO_3 . A similar procedure is used for the synthesis of TiO_2 by the use of titanium salt [21].

2.3. Synthesis of CaTiO_3

CaTiO_3 sample was synthesized by weighing calcium oxide, titanium oxide, and PEG in the ratio 1:1:5 and grounded well in a pestle and mortar. The resultant solid is transferred into a china dish and heated in an open-air atmosphere. The treatment is continued until the carbonaceous fumes completely evolved. Then, it is transferred into a silica crucible and ignited at 1200°C . It was observed during the combustion process that, initially PEG melted, then frothed, and finally gives CaTiO_3 as a residue sample [22]. The obtained final product is given in Figure 1, and its synthetic scheme is given in Scheme 1. The possible reaction involved is given below



2.4. Synthesis of PVA/ CaTiO_3 Composite Film

About 2 g of PVA polymer is weighed and dissolved in water solvent with continuous stirring. The emulsion of PVA polymer was formed, to which 0.1 g CaTiO_3 obtained by combustion method was added. Stirred the solution and poured into the Petri dish, cooled under room temperature until the solvent evaporated to form a thin film to get a uniform-shaped film. Then, a thin film of PVA/ CaTiO_3 composite formed was characterized by various characterization tools.

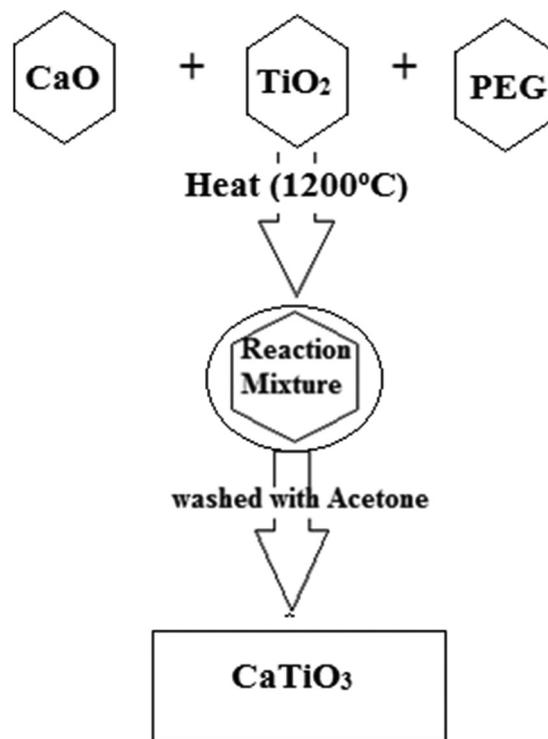


Figure 1: Optical image of combustion-derived CaTiO_3 .

3. RESULTS AND DISCUSSION

3.1. X-Ray Diffraction (XRD) Study

The structure of the prepared CaTiO_3 nanoparticles and its PVA composite samples were confirmed by XRD analysis. Figure 2 represents the XRD pattern of as-prepared CaTiO_3 nanomaterial. The pattern shows various Bragg's reflections due to the crystalline nature with the spinal structure of the sample. Obtained d-spacing values of the sample match well with the JCPDS file of CaTiO_3 nanomaterials. It is clearly indicating that the sample confirms the formation of the spinal CaTiO_3 phase. The crystallinity and phase formation of the synthesized PVA/ CaTiO_3 were examined again by XRD analysis. Figure 3 shows the XRD pattern of solvent-casted PVA/ CaTiO_3 nanocomposite film. The pattern shows the limited Bragg's reflections due to the formation of partial crystallinity nature; also some particles are masked in the PVA matrix. Further, the traced crystallinity in the PVA is due to matrixes of CaTiO_3 nanomaterial. The appearance of CaTiO_3 reflections in the PVA composite sample (peaks are indexed) confirms the formation of the PVA/ CaTiO_3 nanocomposite.



Scheme 1: Synthesis of CaTiO_3 nanoparticles.

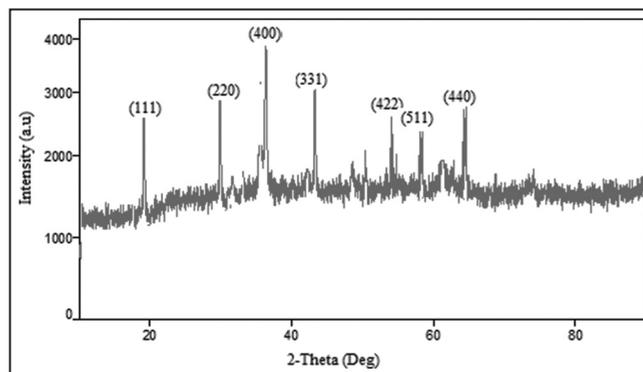


Figure 2: X-ray diffraction pattern of CuAl_2O_4 nanoparticles.

3.2. Fourier-Transform Infrared (FT-IR) Study

The bonding nature of the prepared composites was studied by FT-IR instrumentation. Figure 4 shows FT-IR spectra of as prepared PVA/CaTiO₃ nanocomposite sample. The bands in the region 1000–1150 cm⁻¹ are due to the in-plane bending vibration of the C-H mode. The band at 850 cm⁻¹ originates out-of-plane C-H bending vibration. The spectrum of the polymer composites shows two peaks at 750, 650, and 500 cm⁻¹, which are attributed due to the presence of the CaTiO₃ sample in the poly(vinyl) nanocomposite [23].

3.3. Scanning Electron Microscope (SEM) Study

The scanning electron purchased instrumentation route is to study the surface morphology of the prepared polymer nanocomposite sample. Figure 5 shows the SEM image of the as-prepared PVA/CaTiO₃ nanocomposite film. The image revealed the spherical shape of the particles indicating the semicrystalline nature of the composite sample, and a cluster of differently shaped particles is viewed in the image. In continuation, a particle grouping can also view in the sample image. Some particles masked in the polymer matrix with streak-like arrangement show the reduced crystallinity of the CaTiO₃ sample, and also the development of crystalline nature in the polymer was confirmed by observing particle contacts, which is observed in the SEM image.

3.4 Transmission Electron Microscopy (TEM) Study

Particle morphology and particle size of the prepared PVA/CaTiO₃ nanocomposite film sample were well investigated by transmission

electron microscope study and is given in Figure 6. TEM micrograph image of the composite sample representing the semicrystalline morphology with irregular particles in shape and falls within the nanorange (100 nm). CaTiO₃ nanomaterials are dispersed in the PVA matrix, and some are masked in the PVA matrix. The complex image is showing particle compactness within the matrix range, which is also observed in the image.

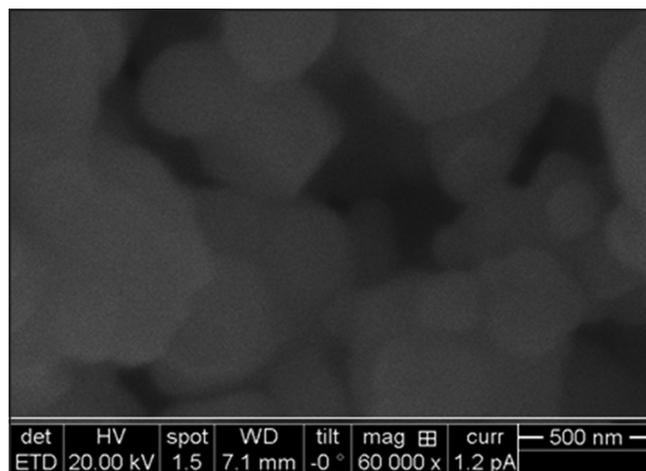


Figure 5: Scanning electron microscope image of poly(vinyl alcohol)/CuAl₂O₄ nanocomposite.

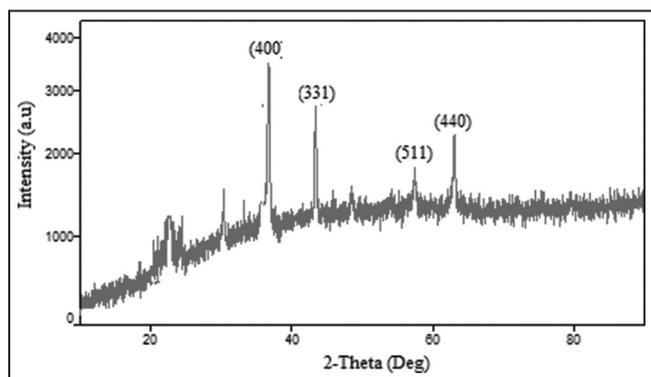


Figure 3: X-ray diffraction pattern of poly(vinyl alcohol)/CuAl₂O₄ nanoparticles.

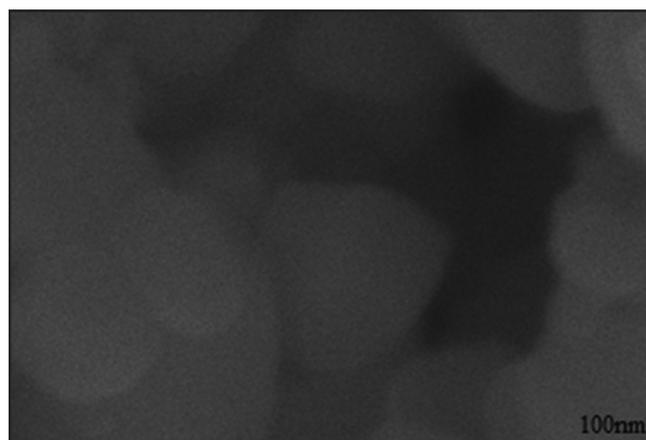


Figure 6: Transmission electron microscopy image of poly(vinyl alcohol)/CaTiO₃ nanocomposite film.

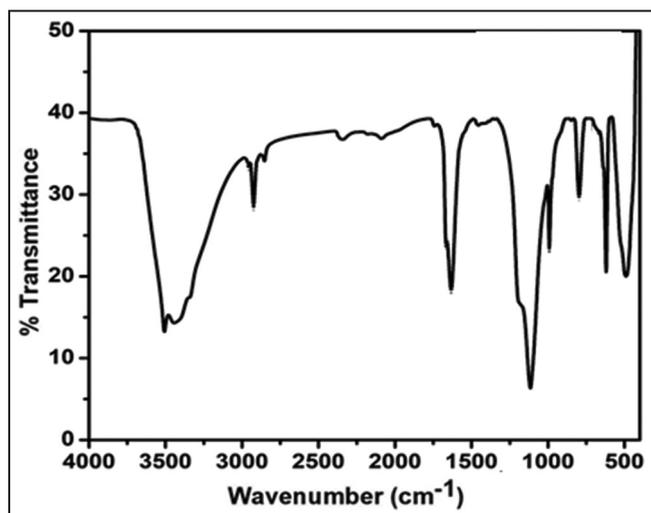


Figure 4: FT-IR of poly(vinyl alcohol)/CaTiO₃ nanocomposite film.

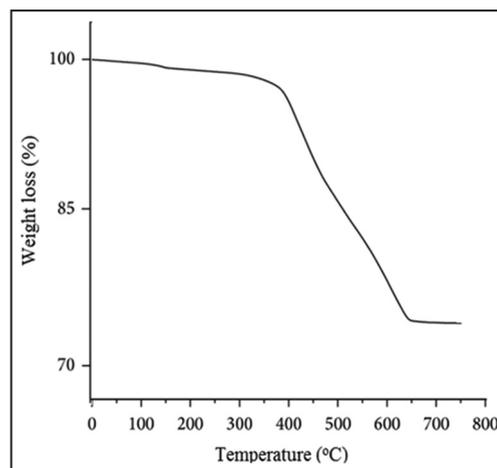


Figure 7: Thermogravimetric analysis image of poly(vinyl alcohol)/CuAl₂O₄ nanocomposite.

3.5. Thermal Study

The thermal stability of the prepared composite was studied by thermogravimetric analysis (TGA). Figure 7 shows the TGA trace of as prepared PVA/CaTiO₃ nanocomposite film. The thermal trace shows the thermal degradation of PVA occurs at 410°C with the initial weight loss at a lesser temperature indicating the release of water moiety of the composite sample. Weight loss occurring around 425°C–600°C is due to the decomposition of the polymer sample due to the strong interaction between CaTiO₃ and PVA.

4. CONCLUSION

Nanocomposite preparation by solvent casting method is a simple and yields phase-formed product. Uniform dispersion of the CaTiO₃ nanomaterials in the PVA matrix forms its nanocomposite film. The developed crystallinity of the composite film was confirmed by the XRD tool. The interaction between CaTiO₃ nanomaterials and PVA was well understood by the FT-IR tool. TEM and SEM studies reveal the applicable morphology and particle size of the samples. The thermal stability of the composite film is confirmed by the thermal gravimetric tool.

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*Bibliographical Sketch



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