IARJSET

ISSN (O) 2393-8021, ISSN (P) 2394-1588

International Advanced Research Journal in Science, Engineering and Technology

Impact Factor 7.105 ⋇ Vol. 9, Issue 3, March 2022

DOI: 10.17148/IARJSET.2022.9336

Mechanical Properties of PVA-ZnO and PVA–CeO_2 nanocomposite films

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Abstract: Mechanical properties of pure Poly Vinyl Alcohol (PVA), PVA-9wt% ZnO, PVA-2.5wt% CeO_2 and PVA-25wt% CeO_2 nanocomposite films prepared by traditional solution casting technique were studied using Universal Testing Machine (UTM) to elucidate various parameters like tensile strength, Young's modulus, percentage of elongation at the break to understand the mechanical strength of these materials. Nano ZnO and nano CeO_2 used as fillers were prepared by cost effective low temperature solution combustion method. The crystallinity and surface morphology and nature of dispersion of nano fillers in these films were ascertained by X-ray diffraction (XRD) and Scanning electron microscopy (SEM) respectively. The studies reveal an increase in tensile strength and Young's modulus of the material in nano CeO_2 doped composite films compared to the host PVA polymer matrix. Whereas, nano ZnO doped composite films showed a slightly decreased value compared to pure PVA. The maximum tensile strength and highest Young's modulus is found in PVA-25wt% CeO_2 nanocomposite films, indicating higher mechanical strength which is attributed to special morphological and microstructural changes in these films which is evident from the SEM images.

Keywords: Mechanical Properties, Tensile strength, modulus of elasticity, nanocomposites, XRD

1. INTRODUCTION

Polymer nanocomposites represent a new alternative to conventionally filled polymers. Because of the Nano sizes of the fillers, filler dispersed nanocomposites exhibit markedly improved optical, dielectric, thermal and electrical properties, increased elastic modulus and strength, outstanding barrier properties and decreased flammability properties when compared to the pure polymers or their traditional composites. Among the various polymers, Polyvinyl Alcohol(PVA) is a very versatile synthetic polymer that has large scale technological applications owing to its polar and semi-crystalline nature. Various research groups have worked towards optical, optoelectronic, electrical, thermal, mechanical and many more properties of Poly vinyl alcohol(PVA) doped with Nanofillers such as ceramics, metals, metal oxides, semiconductors and so on and revealed how a new composite material with improved properties can be realized in various technological applications [1-26].

CeO_2 is an insulating metal oxide in bulk form. However, when used as a nano particle it shows an increase in conductivity, UV-Visible absorbance, good luminescence and so on [25,27,28]. On the other hand, ZnO which is semi-conducting as a bulk has shown also an insulating behaviour in the nano regime [29]. The use of these nanoparticles as a filler to form nanocomposite films has been reported to give rise to improved dielectric, optical, thermal and mechanical properties. In our earlier work we have studied the dielectric, optical, thermal and sensing properties [22-26] of nanocomposite films prepared with the above two nanoparticles doped in the polymer PVA, as a function of the concentration of the filler (5wt%, 9wt%, 13wt% and 17wt% of ZnO) and ((2.5 wt%, 5 wt%, 7.5 wt%, 12.5 wt% and 25 wt% of CeO_2). The studies revealed PVA-9wt% ZnO exhibiting optimum photoluminescence, maximum conductivity, improvised thermal stability and enhanced sensing behaviour among all the ZnO series nanocomposite films. Whereas, among all the CeO_2 series nanocomposite films, PVA-2.5wt% CeO_2 exhibited optimum values in these properties and also PVA- 25wt% CeO_2 showed good thermal stability owing to their special morphological changes forming as nanoribbon or nano bead like structure evident from the SEM and TEM analysis[25]. Henceforth in our present work, we have prepared nanocomposite films of these concentrations (PVA-9wt% ZnO, PVA-2.5wt% CeO_2 and PVA-25wt% CeO_2) which exhibit optimum enhancement in their optical, electrical, thermal and sensing behaviour to ascertain their elastic modulus and tensile strength to understand their mechanical behaviour.

2. EXPERIMENTAL

Synthesis of nanoparticles, pure PVA and nanocomposite films were carried out using Analar grade materials. To synthesize ZnO nanoparticles, a precursor material Zinc nitrate [Zn $(NO_3)_2$, $6H_2O$] was purchased from CDH Ltd., India and a fuel Oxalyl di-hydrazide (ODH) [$C_2H_6N_4O_2$] was prepared in the lab according to the instructions given in the book

DOI: 10.17148/IARJSET.2022.9336

[30]. Whereas, for the preparation of CeO_2 nanoparticles, a precursor material Cerium nitrate ($Ce(NO_3)_3.6H_2O$) and a fuel citric acid ($C_6H_8O_7$) were purchased from CDH Ltd., India. Polymer Poly vinyl alcohol (PVA) with an average molecular weight of 125,000 and 98% hydrolyzed was procured by Aldrich and was used as received. Prepared nanoparticles were uniformly dispersed in polymer matrix by using Cole-Parmer USA, Ultrasonic Processor. Doubly distilled water was used to make all the reactant solutions.

2.1 Synthesis

2.1.1 Synthesis of ZnO and CeO_2 nanoparticles

ZnO nanoparticles were prepared using a quicker, low-temperature solution combustion method using Zinc Nitrate as precursor and ODH as unique fuel. Whereas CeO2 nanoparticles were synthesized using cerium nitrate as an oxidizing agent and citric acid as a fuel. The detailed preparation procedures of both nanoparticles are reported elsewhere [22,25].

2.1.2 Synthesis of PVA, PVA- ZnO and PVA- CeO_2 nanocomposite films

Pure PVA, PVA-9wt%ZnO, PVA-2.5wt%CeO_2 and PVA-25wt%CeO_2 nanocomposite films were prepared by cost effective solution casting method. The details of the method are reported in our earlier work. The pure and composite films were cut into pieces suitable for measurement. The thickness of the films was measured accurately by an optical method using an Air Wedge and was found to be 180 μm /100 μm within the experimental error limit of ±1%.

2.1.3 Characterization

The X-ray diffraction (XRD) patterns of Pure PVA, PVA-9wt%ZnO, PVA-2.5wt%CeO_2 and PVA-25wt%CeO_2 polymer nanocomposite films were recorded at room temperature using an X-ray powder diffractometer with CuK_α radiation (λ = 1.5406 Å) in the 2θ (Bragg angles) range ($10° \leq 2\theta \leq 80°$), to obtain the information related to phase purity, crystallinity and details of their structure. The in-depth X-ray diffraction study of pure PVA and both nano ZnO and nano CeO_2 doped composite films were reported elsewhere [22, 25]. Here the analysis repeated for these particular samples reconfirmed the earlier results. The surface roughness and morphology of these samples were analyzed using a scanning electron microscope (ULTRA 55). A micro universal testing machine (LLOYDS—5 KN, London, UK) was used to measure tensile strength, elongation percentage (%), and modulus of elasticity. The tests were carried out according to ASTM D-882 standard test (ASTM, 1992) and calculated using NEXYGEN Plus software. Square shaped samples of films $0.0027m^2$ area were taken for the determination of tensile properties.

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction Analysis

The depth analysis of X-ray diffraction spectra of Pure PVA, PVA-ZnO nanocomposites for various concentrations of nano ZnO and PVA-CeO2 nanocomposites for various concentrations were reported in our earlier work [22, 25]. Here again, the XRD spectra of samples prepared for the study of mechanical properties were recorded and found to agree with the earlier results. The XRD pattern of pure PVA shown in Figure 3.1(a), exhibits a relatively broad peak centred on 2θ = 20.10° with (1 0 1) plane of crystalline PVA and two more peaks at 2θ = 27.85° and 2θ = 29.20° indicating the semi-crystalline nature of the PVA [22].

Figure 3.1(b) showing the XRD pattern of PVA– 9wt% ZnO nanocomposite films indicates many additional peaks when compared with pure PVA, which are attributed to the reflection planes of the ZnO hexagonal Wurtzite crystal structure [22]. These peaks assure the formation of PVA– ZnO hybrid composite with the development of high crystallinity in the PVA matrix due to the complexation of metal oxide nanoparticles with it.
The XRD patterns of PVA-2.5wt%CeO_2 (Fig. 3.1c) and PVA-25wt%CeO_2 (Fig. 3.1d) nanocomposite films show many additional peaks when compared to pure PVA, some of which corresponds to peaks in the XRD of nano CeO_2 [25] establishing the complexation of metal oxide nanoparticles with PVA in the hybrid films.

IARJSET ISSN (O) 2393-8021, ISSN (P) 2394-1588

International Advanced Research Journal in Science, Engineering and Technology

Impact Factor 7.105 ⁑ Vol. 9, Issue 3, March 2022

DOI: 10.17148/IARJSET.2022.9336

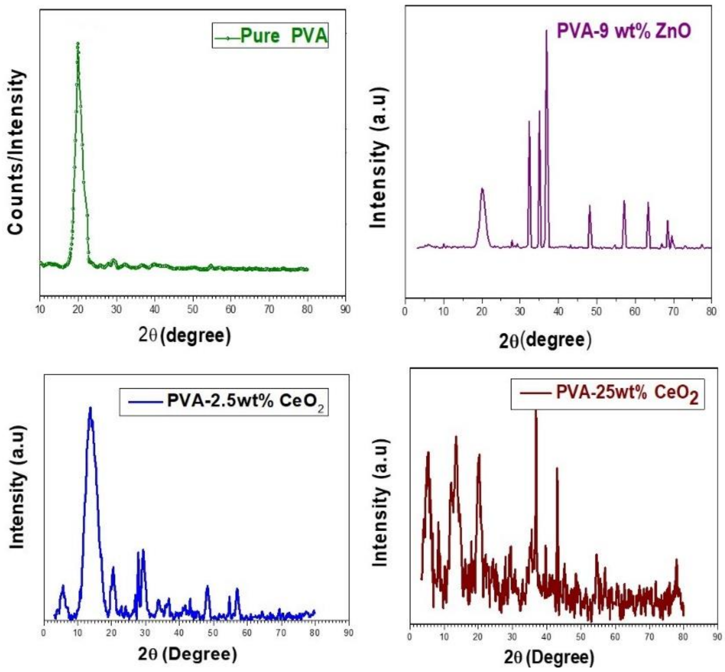

Figure 3.1. XRD spectra of pure PVA and nanocomposite films

Figure 3.1(c) shows an increase in the degree of crystallinity of the nanocomposite with the inclusion of filler CeO_2. Whereas, a composite film with the highest concentration of nanofiller (25wt%CeO_2) exhibit a larger decrease in intensity of these lines indicating to be non-existent while the visible peaks correspond to PVA alone. These have also increased in number pointing to the complexation of CeO_2 with PVA. The results reconfirm the reported analysis elsewhere [22, 25].

3.2 Scanning electron microscopy

The SEM micrographs of pure PVA film, PVA– 9wt% ZnO film, are shown in Figure 3.2. SEM of pure PVA at low magnification shows (Figure 3.2(a)) the semi-crystalline nature of PVA supporting the observations of XRD analysis. Whereas hybrid film reveals the uniform distribution of filler nano ZnO in hos polymer PVA matrix confirming the interaction between the two.

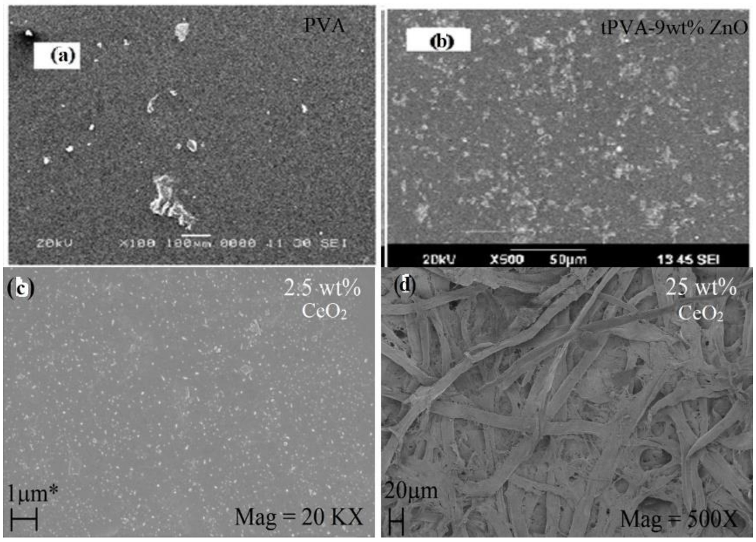

Figure 3.2 SEM spectra of pure PVA and nanocomposite films.

The SEM images of PVA-2.5wt%CeO_2 show uniformly dispersed nano CeO_2, with a relatively rough surface compared to pure PVA. The 25wt% CeO_2 concentration Figure 3.2(d) looks different from the other films with some fibrous tape

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like structures. This structure looks like a precursor to nanoribbons along with a porous nature and is seen to affect the mechanical properties investigated in these films. The results observed in SEM spectra of all these samples is similar to detailed analysis carried out in various concentrations of ZnO and CeO_2 doped PVA hybrid films reported elsewhere and also validates the repeatability of results.

3.3 Mechanical properties

Mechanical properties were studied to explore the tensile properties of pure PVA, ZnO and CeO_2 doped composite films by using Universal Testing Machine (UTM). The sample films were placed between two metallic grips, wherein the lower grip was held stationary and the upper grip moves upward with the consistent extension of 2.5mm/minute such that constant initial grip separation was maintained for all the samples. The constant speed of the upper grip was recorded by an automatic speed controller fixed to it. The UTM is an electrically driven system. All measurements were performed at ambient temperature conditions in the air medium.

To ascertain the good quality of the material for its long-lasting performance or failure, various tensile parameters like tensile strength, Young's modulus (modulus of elasticity), elongation percentage was measured which links its chemical structure with the exhibited mechanical properties of the samples.

The observation from the Figure. 3.3 and Table 1 reveals the existence of the highest tensile strength in PVA-25wt% CeO_2 nanocomposite films and lower strength in PVA-9wt% ZnO nanocomposite films compared to pure PVA. The highest tensile strength is attributed to a high molecular weight of the polymer which brings in the effect of entanglement. The morphological changes and the extent of increase in crystallinity in these composite films account for the significant effects on the mechanical behaviour of the polymer films. The increase in crystallinity due to secondary bonding, in turn, increases stiffness and elastic modulus and strength of the polymer. The maximum percent total elongation at fracture was found for PVA doped with 2.5wt% CeO_2. Elongation at break is the highest change in length of a test film before breaking. The results indicate the significant increase in mechanical strength of the host polymer PVA when it is doped with 25wt% CeO_2 evident by an increase in tensile strength, maximum stiffness and Young's modulus as depicted in Figure 3.3 and Table1.

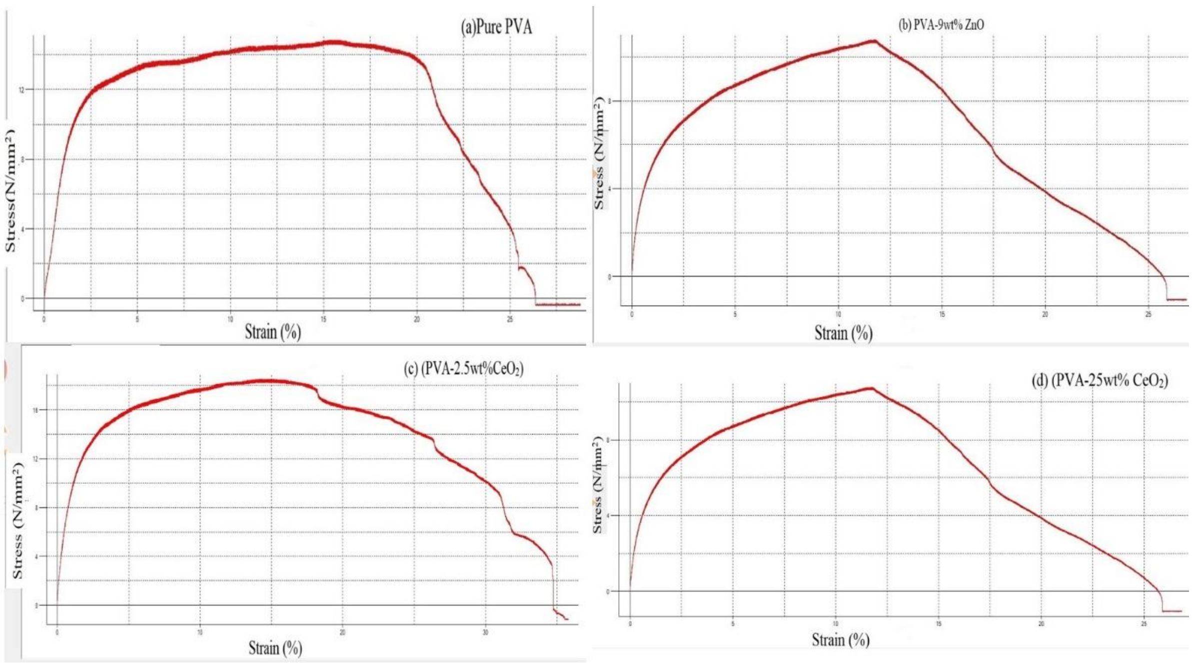

Figure 3.3. Variation of Stress versus strain percent of pure PVA and nanocomposite films.

Table 1. Tensile properties of pure PVA and nanocomposite films:

Sample	Tensile strength (Mpa)	Stiffness (kN/m)	Young's modulus (Mpa)	Percentage (%) total elongation at fracture
Pure PVA	14.84	7.35	259.85	24.41
PVA-9wt% ZnO	10.78	12.46	213.07	14.57
PVA-2.5wt% CeO_2	18.55	34.78	742.01	23.63
PVA-25wt% CeO_2	18.00	57.97	1236.49	12.46

DOI: 10.17148/IARJSET.2022.9336

ZnO in the nano regime has shown lower mechanical strength as reported by various researchers [31]. Thus inclusion of nano ZnO in PVA has shown decreased tensile strength and lower Young's modulus compared to pure PVA which is revealed from the tabulated values.

CONCLUSIONS

The nanocomposites films prepare for various concentrations of ZnO and CeO2 doped to polymer PVA were studied for their morphological and crystallinity properties using SEM and XRD. Among PVA-9wt%ZnO, PVA-2.5wt%CeO_2 and PVA-25wt%CeO_2 polymer nanocomposite films, PVA-25wt%CeO_2 polymer nanocomposite films, exhibit the highest tensile strength and Young's modulus confirming the greater mechanical strength of the nanocomposite films compared to pure PVA.

ACKNOWLEDGEMENT

Author KSH thanks the **CeNSE IISc,** for the UTM and SEM measurements. The authors also thank **STIC, Cochin, Kerala,** for the XRD characterization facility.

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