



Optoelectronic Behaviors of Reversibly Stretchable $\text{Na}_{0.8}\text{Mn}_{0.8}\text{O}_2$ Reinforced Poly (Vinyl Alcohol) Nanocomposites

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Abstract:

Herein, we report the fabrication of highly flexible polyvinyl alcohol (PVA) nanocomposites with solution combustion developed sodium-doped manganese dioxide ($\text{Na}_{0.8}\text{Mn}_{0.8}\text{O}_2$) nano fillers by aqueous solution casting. The as developed nanocomposite systems were studied for their morphological, optical and electrical behaviors. The structural and morphological behaviors of PVA/ $\text{Na}_{0.8}\text{Mn}_{0.8}\text{O}_2$ nanocomposite films were characterized by Fourier Transform Infrared (FTIR) and scanning electron microscopy (SEM), while dielectric properties and ac conductivities were established using LCR meter. The optical response of PVA and its nano filler fabricated analogues were probed by UV-visible spectral studies. The general behavior showed that dielectric constant (ϵ) decreased with increasing frequency. The introduced filler affects an obvious decrease in the energies associated with inter-band electronic transitions leading to novel material properties. The charge transport properties valued by dielectric studies validate a filler dependent electronic response with electrical conductivities showing a monotonic dependence on filler content. The developed films with high dielectric constant and appreciable charge dissipation alongside high flexibility and reversible stretchability are of potential interest in microelectronics.

Key words: Dielectric studies, Vibrational spectra, Electrical conductivity

I. INTRODUCTION

Research on stretchable electronic systems is motivated by the want for electronic systems that are able to sustain large mechanical strain to operate under real-time outdoor environments. Such stretchable electronic systems are found to be handy in applications involving polymer light-emitting diodes, mechanical strain sensors, electrical transistors and so forth. The field of stretchable electronics can only be realized in the presence of a stretchable power source. In recent years, there has been increasing interest towards the design and development of stretchable energy storage systems for super capacitor applications. Supercapacitors are fascinating energy storage devices that present the advantage of charging and discharging within instants, alongside storing a larger portion of electrical current similar to chemical batteries.¹ additionally, super capacitors also offer high power densities and long cycle stabilities. Furthermore, it is highly desirable to integrate optical transparency with mechanical stretchability within a single device to realize unique applications such as aesthetically pleasing wearable electronics in addition to integrated energy harvesting and storage systems. Thus, polymeric composites that are essentially a synergistic combination of opto-electrically effective inorganic nanofillers and highly processable organic polymer may open up the technological gateway towards the realization of optical transparent flexible electronics for optoelectronic applications. In addition, polymeric composites are also known to offer excellent thermal stabilities to suit real-time outdoor applications. Thus, in the present work an attempt is made to fabricate optical transparent poly (vinyl alcohol) (PVA) with nano sized sodium-doped manganese dioxide ($\text{Na}_{0.8}\text{Mn}_{0.8}\text{O}_2$) dielectrics, so as to effectively harness the processability and optical transparency of PVA alongside the dielectric behaviors

of inorganic nanofillers. Poly (vinyl alcohol) is chosen as the matrix material owing to its –OH backbone that aids particle stabilization in addition to its very high dielectric strength (41000 kV/mm) and dopant dependent opto-electronic behaviors.^{2,3} While, manganese dioxide is an established dielectric, which when doped with suitable alkali metal may aid increased dielectric performance. Thus, in the present work, an attempt is made to understand the dielectric conduction and relaxation mechanisms of PVA/ $\text{Na}_{0.8}\text{Mn}_{0.8}\text{O}_2$ nanocomposites for electrical energy storage applications.

II. EXPERIMENTAL MATERIALS

PVA with a weight average molecular weight of 124,000 (86–89% hydrolyzed) was obtained from SD Fine Chemicals, India. While, the precursors employed for the synthesis of $\text{Na}_{0.8}\text{Mn}_{0.8}\text{O}_2$ nanostructures, viz., Manganese nitrate ($\text{Mn}(\text{NO}_3)_2$, sodium nitrate (NaNO_3) and glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) were procured from Loba Chemie, India, Nice Chemicals, India and SD Fine Chemicals, India, respectively.

Synthesis of $\text{Na}_{0.8}\text{Mn}_{0.8}\text{O}_2$ by solution combustion

$\text{Na}_{0.8}\text{Mn}_{0.8}\text{O}_2$ nanoparticles were synthesized by previously established solution combustion (SC) technique. Solution combustion involved an exothermic reaction initiated by heat that becomes self-sustaining within a certain time interval resulting in fine powders. The desired nano metal oxides were synthesized with $\text{Mn}(\text{NO}_3)_2$ and NaNO_3 as oxidants and nitrogen rich glycine as fuel source. In a typical synthesis, 0.169g sodium nitrate, 2.01g manganese nitrate and 0.150g glycine were dissolved in 25 ml of distilled water under constant stirring. The resulting mixture was then placed on a hot plate (~95 °C), which underwent auto ignition, leaving behind fine powder. The powders so obtained were then annealed at 400 °C in a muffle furnace for 2 hrs.

Development of PVA/Na_{0.8}Mn_{0.8}O₂ nanocomposite

PVA/Na_{0.8}Mn_{0.8}O₂ nanocomposite films were developed by aqueous solution casting technique.⁴ In a typical film formation process, 7.5 wt% aqueous PVA was prepared by dissolving 100ml distilled water under constant stirring. The solution combusted Na_{0.8}Mn_{0.8}O₂ nanofillers were then dispersed in aqueous PVA by ultrasonication to ensure uniform filler dispersions. The homogenized solution was then poured onto pre-cleaned glass molds and air dried at room temperature.

III. CHARACTERIZATION

The average particle size of Na_{0.8}Mn_{0.8}O₂ nanofillers were ascertained by Dynamic Light Scattering (DLS) technique using LS nanolab particle size analyzer, Switzerland. The vibrational spectra of PVA nanocomposites were recorded in the spectral range of 4000-400cm⁻¹ using JASCO 4100 Fourier Transform Infrared (FTIR) spectrometer, Japan. The X-ray powder diffraction (XRD) instrument, Bruker XRD in the scanning range 10-60° (CuK_α radiation; λ = 1.54Å) was employed for identifying the changes in the crystalline phases of PVA nanocomposite film. The electronic spectral studies were affected by Shimadzu-1800 spectrophotometer, Japan. While, the electrical conductivity and dielectric measurements were affected as per ASTM-150 standards in the frequency range 100Hz– 5MHz under a static operating voltage of 1V using Hioki LCR HiTESTER 3532-50, Japan. The thermo gravimetric behaviors were analyzed using Waters Cienna Q600SDT and Q-20DSC TGA instrument, Australia.

IV. RESULTS AND DISCUSSIONS

Assertion of Na_{0.8}Mn_{0.8}O₂ domain size

Dynamic Light Scattering (DLS) technique was employed to characterize the size of Na_{0.8}Mn_{0.8}O₂ nano fillers. DLS measures the scattered light from the colloidal Na_{0.8}Mn_{0.8}O₂ dispersions by analyzing the modulation of scattered light. The DLS profile of solution combustion synthesized Na_{0.8}Mn_{0.8}O₂. Figure. 1 shows the typical size distribution with majority of the particles having an average domain size of 60nm.

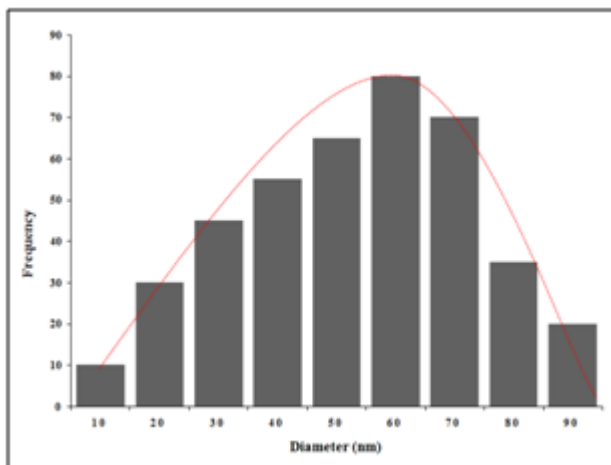


Figure.1. Particle size distribution of solution combusted Na_{0.8}Mn_{0.8}O₂

FTIR Studies

Fourier Transform Infrared (FTIR) spectra of pure PVA and its nanocomposite films were recorded in ATR mode to explore the nature of interactions between the nano-sized filler and -OH groups of PVA. The FTIR for pure PVA and 4wt% PVA/Na_{0.8}Mn_{0.8}O₂ nanocomposite film is shown in Figure. 2.

The vibrational spectra of undoped PVA films reveal infrared characteristics peaks of hydroxyl backbone of PVA matrix. The IR spectrum of PVA and its nanocomposite films exhibit a broad and strong band around 3500–3095 cm⁻¹ corresponding to the -OH stretching vibrations of PVA backbone. However, the nano filler introduced composite films exhibit appreciable changes and peak intensities corresponding to -OH groups owing to the electrostatic interactions between Na_{0.8}Mn_{0.8}O₂ nano filler and hydroxyl groups of PVA. The peak around 1767–1680 cm⁻¹ is due to the residual acetate groups of PVA (partially hydrolyzed poly (vinyl acetate) (PVAc). The absorption band occurring around 2973–2886 cm⁻¹ corresponds to asymmetric stretching mode of -CH₂ group, while the peak at 1525–1478 cm⁻¹ corresponds to C-H bending of -CH₂ group in the PVA backbone. A band at 1276–1258 cm⁻¹ corresponds to wagging of -CH₂ group. The momentous shift in the peak position and intensities corresponding to C=O (crystalline) and C-O-C stretching vibrations of PVA indicates a positive interaction between -OH groups of PVA and nanofiller. The appearance of an additional absorbance band at 565–525 cm⁻¹ in the IR spectra of PVA/Na_{0.8}Mn_{0.8}O₂ nanocomposite films may be attributed to metal-oxygen stretching, which in turn justifies the existence of nanoparticles in PVA matrix. The shift in acetyl C-O-C stretching of PVA also supports the existence of chemical interaction between the metallic nano filler and PVA. Furthermore, the tapering off the -OH stretching band with an increase in dopant concentration also supports the strong tendency of -OH groups of PVA to form charge-transfer complexes with metal oxide nanofillers through chelation.^{2,4}

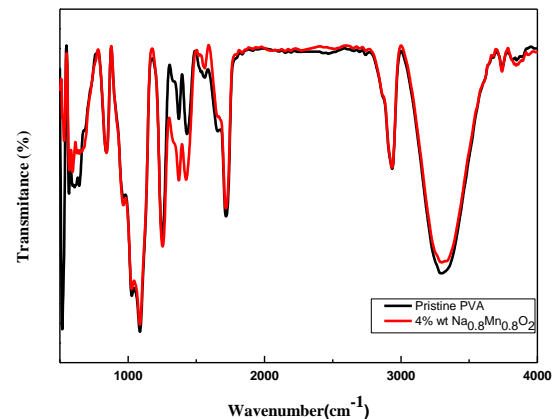


Figure.2. FTIR spectra of PVA/Na_{0.8}Mn_{0.8}O₂ nanocomposite films

Electronic spectral studies

The electronic spectral studies ascertain the formation of charge transfer interactions between Na_{0.8}Mn_{0.8}O₂ nano fillers and -OH groups of PVA with electronic band structure of PVA showing an appreciable change with the addition of nano fillers. The changes in the band structure of composite films leads to decreased optical band gaps and hence increased charge conduction.⁵⁻⁷ The optical band gap studies are in accordance with the UV-visible absorbance studies that perceive an increase in photonic absorption with increasing nano filler content that induces higher charge conduction. The decrease in optical band gap of PVA upon Na_{0.8}Mn_{0.8}O₂ nano filler introduction is in line with absorption co-efficient measurements that show an appreciable shift in the absorption edge (Figure.3) towards lower energy/higher wavelengths reflecting the variation in electronic band structure of PVA due to changes in the crystal structure of polymeric host upon doping. The decrease in the optical band of Na_{0.8}Mn_{0.8}O₂/PVA

nanocomposite systems facilitate an easier conduction pathway for the charges to transit leading to increased charge conduction, as discussed in subsequent sections.^{8,9}

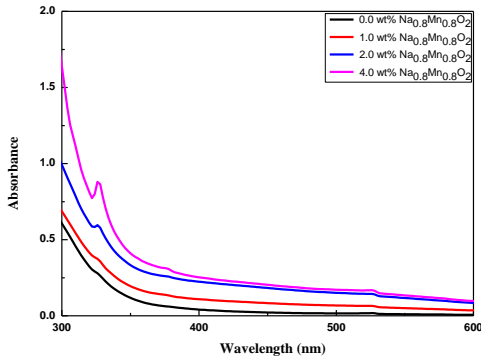


Figure.3. UV-visible absorbance spectra of PVA/ Na_{0.8} Mn_{0.8}O₂ nanocomposite films

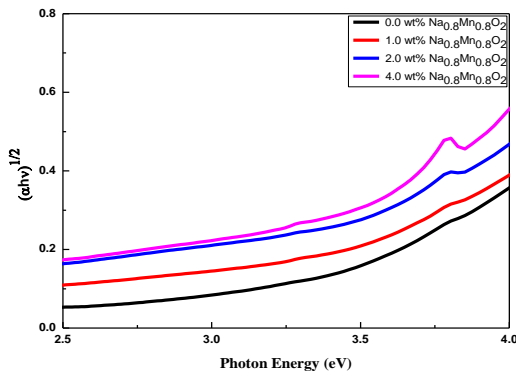


Figure.4. Optical band gap of PVA/Na_{0.8}Mn_{0.8}O₂ nanocomposite films

X-Ray Diffraction Studies

The X-ray diffraction analysis sheds light on the changes in crystal phases and micro structural behaviors of polymeric films upon doping. As can be seen from Figure. 5, all the films under investigation display a broad shoulder peak at scattering angles ($19^\circ < 2\theta < 20^\circ$) and d-spacing value of 4.38\AA corresponding to (101) crystal plane of semicrystalline PVA.¹⁰⁻¹² However, the Na_{0.8}Mn_{0.8}O₂ nanofillers introduced composite films show additional diffraction peaks at 2θ values of 28.7° , 33.1° and 35.5° validating the presence of inorganic nano fillers in the organic host. The observed changes in the micro structural behaviors may to changes in the electronic band structures and hence the energies associated with HOMO-LUMO electronic transitions.

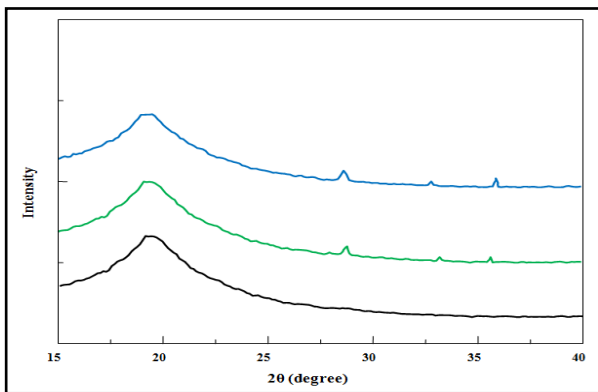


Figure.5. XRD patterns for PVA/Na_{0.8}Mn_{0.8}O₂ nano composites containing (a) 0, (b) 2.0 and (c) 4.0 wt% Na_{0.8}Mn_{0.8}O₂ nanoparticles

Electrical properties of nanocomposite films

Increase in conductivity validates the presence of Na_{0.8}Mn_{0.8}O₂ in the PVA matrix. The change in conductivity values observed at low frequency region for all PVA/Na_{0.8}Mn_{0.8}O₂ nanocomposite films are due to the electrode polarization. Furthermore, the addition of Na_{0.8}Mn_{0.8}O₂ nanofiller improves the polarity of the PVA matrix.^{4,15} As the frequency increases, electrons are sufficiently energized and hop from one conducting cluster to another through smaller inter-particle gaps. Hence, there is a significant improvement in conductivities upon increasing the amount of Na_{0.8}Mn_{0.8}O₂ in PVA. From the Figure. 6, it is also evident that the highest conduction is observed for 2.0 wt.% of Na_{0.8}Mn_{0.8}O₂ in PVA. The comparatively low conductivity at 4.0 wt.% of Na_{0.8}Mn_{0.8}O₂ in PVA may be due to the filler agglomeration that limits the ease of charge conduction.²¹⁻²⁴

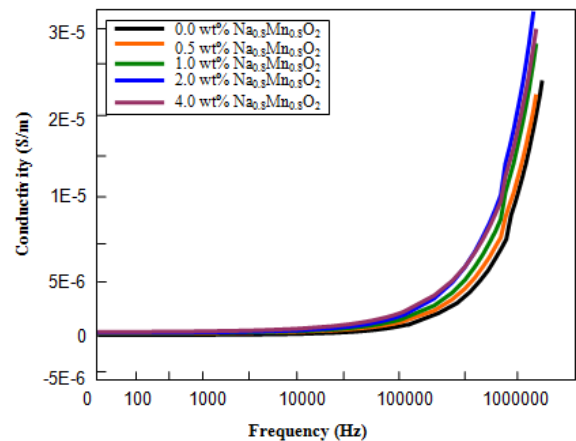


Figure.6. AC conductivity of PVA/Na_{0.8}Mn_{0.8}O₂ nano composites as a function of log frequency

Dielectric constant

The dielectric constant (ϵ) of PVA/Na_{0.8}Mn_{0.8}O₂ films as a function of frequency at room temperature are illustrated in Figure.7. It can be observed that ϵ decreases monotonically with increasing frequency due to the lack of dipolar response. Accordingly, the dielectric loss is high. It is also observed that, the values of ϵ of PVA/Na_{0.8}Mn_{0.8}O₂ increased with increasing amount of Na_{0.8}Mn_{0.8}O₂ nanofillers, owing to interfacial polarization originating in the PVA/Na_{0.8}Mn_{0.8}O₂ interfaces in addition to the formation of mini-capacitor networks in the PVA/Na_{0.8}Mn_{0.8}O₂ nanocomposite with increasing Na_{0.8}Mn_{0.8}O₂ content.^{13, 14, 25}

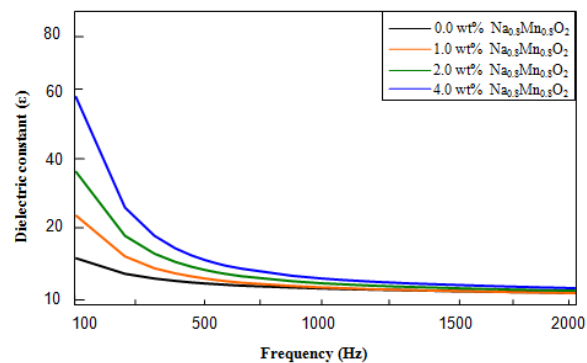


Figure.7. Effect of frequency on the dielectric constant of PVA/Na_{0.8}Mn_{0.8}O₂ nanocomposites

TGA studies

The nano filler fabricated PVA films were subjected to thermo gravimetric analysis (TGA) to probe the thermal

stability of composite films by analyzing the degradation patterns. The thermo grams of PVA/Na_{0.8}Mn_{0.8}O₂ composite systems Figure. 8 substantiate the thermal stabilities of nanocomposite systems, which display increased stability upto 52^oC and underwent complete degradation at 560 ^oC. The TGA thermo grams of all the composite films display a three step thermal degradation, the first step corresponding to removal of moisture and physisorbed moisture, while the second step depicting a major weight loss is most dominant degradation process that involves the elimination of -OH groups and chain-scission reactions. The final step is the ultimate decomposition of polyene residues to yield the carbon dioxide and hydrocarbons. Furthermore, the introduced Na_{0.8}Mn_{0.8}O₂ nanofillers brought about considerable enhancement in thermal stabilities of composite films as inferred from the most important peak degradation (T_p) with maximum weight loss rate.^{20, 26} The T_p is increase from 250 to 270 °C with the addition of nanofiller. The observed increment in thermal stability is due to the introduction of Na_{0.8}Mn_{0.8}O₂ nanofillers that act as barriers materials to neutralize the heat dissipation.

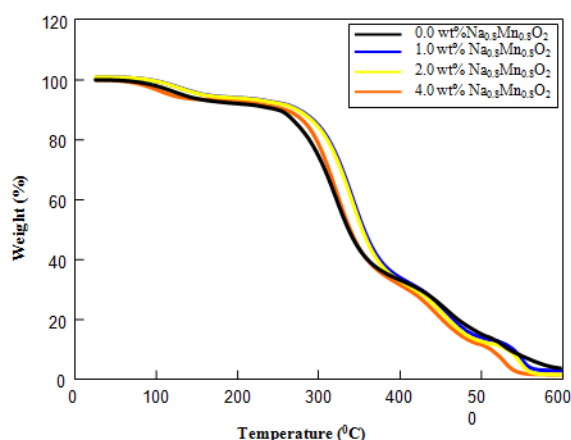


Figure.8. TGA thermo grams of PVA/Na_{0.8}Mn_{0.8}O₂ nano composite samples containing (a) 0, (b) 1.0 and (c) 2.0 and (d) 4.0 wt.% Na_{0.8}Mn_{0.8}O₂

IV. CONCLUSION

PVA/Na_{0.8}Mn_{0.8}O₂ nanocomposite films with varying amounts of Na_{0.8}Mn_{0.8}O₂ content were fabricated by solution intercalation method. The effects of the Na_{0.8}Mn_{0.8}O₂ nanoparticles on the structural, thermal and electrical properties of the nanocomposites were established. It was noticed that the electrical conductivity of the composite films increased with frequency, whereas the dielectric constant decreased with applied frequency. The powder x-ray diffractograms showed the nature interaction between Na_{0.8}Mn_{0.8}O₂ with the PVA matrix. TGA analysis revealed a slight enhancement in the thermal stability of the nanocomposites with increasing nanofiller content. The nanofabricated films shows excellent flexibilities with enhanced charge storage densities to be employed for super capacitor applications.

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