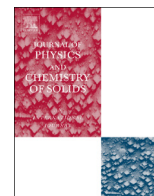




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Influence of lithium potassium zirconate nanoparticles on the electrical properties and structural characteristics of poly(vinyl alcohol) films

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ABSTRACT

We investigated the influence of lithium potassium zirconate (LiKZrO₃) nanoparticles on the electrical properties and structural characteristics of poly(vinyl alcohol) (PVA) films. PVA/LiKZrO₃ nanocomposite films were prepared by casting of aqueous solutions with varying LiKZrO₃ content (0.5, 1.0, and 2.0 wt.%). The dielectric constant (ϵ'), dielectric loss (ϵ''), AC conductivity (σ_{ac}), dielectric loss tangent ($\tan \delta$), and electric modulus (M' and M'') of the nanocomposite films were measured over a range of frequencies at ambient temperature. The results show increases in σ_{ac} and M' with frequency, whereas ϵ' , ϵ'' , and $\tan \delta$ decreased with increasing frequency. The films were also characterized using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and X-ray diffraction (XRD) techniques. DSC and XRD revealed the nature of LiKZrO₃ nanoparticle interaction with the PVA matrix. TGA analysis revealed an increase in thermal stability of the nanocomposites with increasing nanoparticle concentration. Scanning electron microscopy confirmed uniform dispersion of LiKZrO₃ nanoparticles in the PVA matrix.

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1. Introduction

There is increasing research interest in polymeric nanocomposites owing to improvements in electrical, thermal, optical, and mechanical properties [1] and their great potential for highly functional materials [2,3]. In particular, nanoparticles embedded in a transparent matrix have attracted attention as advanced technological materials because of their high transparency, high refractive index [4], and attractive electrical/electronic properties [5]. Metal oxide nanocomposites play a very important role in electrical and optical devices. Polymeric nanocomposites also demonstrate high thermal stability compared to virgin polymers [6]. The thermal stability of nanocomposites governs the mechanical properties, durability, spectral stability, shelf life, and life cycle of polymers [7–11].

In the present study, we selected poly(vinyl alcohol) (PVA) as a transparent host and lithium potassium zirconate (PVA/LiKZrO₃) nanoparticles as a nanofiller. PVA is a water-soluble polymer that allows preparation of nanocomposites film via environmentally friendly aqueous solution casting. PVA films are flexible and show excellent transparency in the visible range, with good dimensional stability. PVA films have high tensile and tear strength and good thermal and chemical resistance [12–14]. PVA has numerous applications in electronics, textiles, and packaging industries, and is extensively used in the fabrication of nanocomposites films [15–18]. PVA films have very high dielectric strength (> 1000 kV/mm) and

good charge storage capacity and dopant-dependent electrical and optical properties. Hence, PVA films are of importance for the microelectronic industry. The electrical properties of PVA nanocomposite films have been extensively investigated [19–22]. Their electrical conductivity depends on thermally generated carriers and dopants [23,24].

It was found that addition of lithium zirconate (Li₂ZrO₃) [25] or sodium zirconate (Na₂ZrO₃) [26] can enhance the dielectric constant, dielectric loss, alternating current (AC) conductivity, and dissipation factor of PVA films. Encouraged by these results, in our ongoing efforts to investigate the influence of metal oxide nanoparticles on the optoelectrical properties of PVA matrices [25–27], we studied the fabrication of PVA and lithium potassium zirconate (PVA/LiKZrO₃) nanocomposite systems. We measured the dielectric permittivity, dielectric loss, and conductivity of PVA/LiKZrO₃ nanocomposites at different frequencies to probe the effect of the filler in the PVA matrix. The structure–property relationship for the nanocomposites was analyzed using differential scanning calorimetry (DSC), X-ray diffraction (XRD), and scanning electron microscopy (SEM) methods. Our primary focus was to explore the potential of LiKZrO₃ metal oxide nanoparticles on the structural and electrical properties of the transparent PVA host.

2. Experimental

2.1. Materials

We obtained PVA with a weight average molecular weight of 124,000 (86–89% hydrolyzed) from SD Fine Chemicals, India.

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Zirconyl nitrate (Loba Chemie), lithium nitrate (SD Fine Chemicals), potassium nitrate (AR, 99.5%; Nice Chemicals) and glycine (SD Fine Chemicals) were used to prepare LiKZrO₃.

2.2. LiKZrO₃ synthesis

LiKZrO₃ was synthesized using the solution combustion (SC) technique. SC is a versatile, simple, and rapid process that allows effective synthesis of a variety of nanosized materials in powder form with good yield. In a typical experimental procedure, 5.79 g of lithium nitrate (LiNO₃), 4.755 g of potassium nitrate (KNO₃), 4.14 g of zirconyl nitrate [ZrO(NO₃)₂], and 4.9 g of glycine (used as a fuel) were dissolved in 125 mL of distilled water. The reaction mixture was placed on a hot plate. As the reaction progressed, water vapor and nitrates (nitric gases) were released, resulting in the formation of a gel. The reaction was completed by self-ignition (combustion) minutes after gel formation, yielding a fine powder. The product was then calcined at 400 °C to produce LiKZrO₃ nanopowder.

2.3. Fabrication of PVA/LiKZrO₃ nanocomposite films

PVA/LiKZrO₃ nanocomposite films were prepared by aqueous solution casting. PVA was dissolved by heating at 95 °C under stirring for 3 h and the calculated amount of LiKZrO₃ was then added under stirring. The solid content of the solution was optimized at 7.5%. Before casting, the solution was sonicated at 90 °C for 30 min. PVA/LiKZrO₃ films were cast from solutions containing 0.5, 1.0, or 2.0 wt.% LiKZrO₃. Cast films were then dried at room temperature for 3 days. This yielded films of 0.10–0.18 mm in thickness that were free from air bubbles and with uniformly dispersed LiKZrO₃ particles. The films were then subjected to annealing at ~60 °C for 2 h for further characterization.

2.4. Characterization

The electrical properties of the PVA composite films were measured according to the ASTM standard using a high-frequency LCR meter (Wayne Kerr model 6500 P) by placing cylindrically molded samples (50 mm in diameter and 0.12 mm thick) between two circular electrodes. DSC thermal analyses were performed using a Mettler Toledo DSC1 STARe system from ambient temperature to 250 °C at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) was performed using a Waters Cienna Q600SDT and Q-20DSC system from ambient temperature to 650 °C at a heating rate of 20 °C/min under nitrogen atmosphere. XRD analysis was performed using a Rigaku Miniflex II desktop diffractometer ($\lambda=1.54 \text{ \AA}$, scan speed 3°/min, 2 θ range 0–60°). Surface images of PVA/LiKZrO₃ films were recorded by SEM (ESEM Quanta 200) at an operating voltage of 10.00 kV.

3. Results and discussion

3.1. Influence of LiKZrO₃ nanoparticles on the dielectric constant of PVA films

The electrical properties of polymeric films containing metal oxide nanofillers are a major field of research because of their novel technological applications. The dielectric constant (ϵ') is a measure of the ability of a material to store electrical energy. The dielectric behavior of a polymer is determined by the charge distribution and statistical thermal motion of its polar groups. The physical structure has a great influence on the dielectric behavior [28]. The dielectric properties of polar materials depend on whether dipoles are attached to the main chain. Dipole polarization depends on segmental mobility. Polar molecules have a high dielectric constant and this depends on temperature

and frequency. The commercial PVA we used is semi-crystalline in nature. The predominantly polycrystalline character of PVA creates a substantial amount of disorder. The dielectric properties of PVA can be improved by addition of metal oxide nanoparticles. The dielectric parameter as a function of frequency is described by the complex permittivity in the form

$$\epsilon^*(\omega) = \epsilon'(\omega) - \epsilon''(\omega), \quad (1)$$

where the real part $\epsilon'(\omega)$ and imaginary part $\epsilon''(\omega)$ are components for energy storage and energy loss, respectively, in each cycle of the electric field. For the dielectric characteristics, the measured capacitance $C(\omega)$ was used to calculate the dielectric constant of the composites according to

$$\epsilon'(\omega) = C(\omega) d/A, \quad (2)$$

where d is the sample thickness and A is its surface area. For the dielectric loss,

$$\epsilon''(\omega) = \epsilon'(\omega) \cdot \tan \delta(\omega), \quad (3)$$

where $\tan \delta$ is the dielectric loss tangent. Then we can use calculated data to determine the dielectric modulus. In complex form, the dielectric modulus is:

$$M^* = 1/\epsilon^* = M' + jM'', \quad (4)$$

where M' and M'' are the real and imaginary parts of the dielectric modulus, calculated as

$$M' = \epsilon' / (\epsilon'^2 + \epsilon''^2)$$

$$M'' = \epsilon'' / (\epsilon'^2 + \epsilon''^2). \quad (5)$$

From M'' , the relaxation time of the dipole orientation can be obtained. The peak for angular frequency, ω_p , can be obtained from a graph of M'' versus log frequency:

$$T = 1/\omega_p. \quad (7)$$

We analyzed the dielectric properties as a function of frequency at ambient temperature. Fig. 1 shows ϵ' as a function of frequency for composite films with different LiKZrO₃ nanoparticle concentrations. It is evident that ϵ' decreases with increasing frequency. The frequency increase restricts the orientation of dipoles and decreases the dielectric constant.

Electrical charges and dipoles in a material respond to the applied field and reorient themselves under the field. The dipole number and density and their size and interaction with each other define the dielectric permittivity of a material. A high dielectric constant at low frequency might be due to electrode and interface effects on the sample [29]. Thus, for polar materials such as PVA the initial value is high, but as the frequency of the AC field increases, ϵ' begins to decrease [30]. Similar trends were observed for PVA/Li₂ZrO₃ [25], PVA/Na₂ZrO₃ [26], and PVA/ZnO-Ce₂O₃ [27].

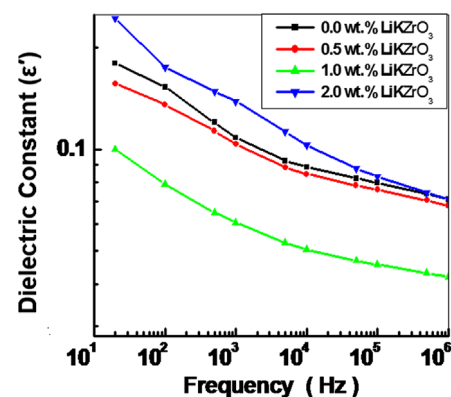


Fig. 1. Effect of frequency on the dielectric constant of PVA/LiKZrO₃ nanocomposites.

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