Preparation and characterization of EVA/ZnO composites as piezoelectric elements for ultrasonic transducers

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Abstract
Films of EVA/ZnO composites prepared to be piezoelectric active elements for ultrasonic transducers. These films are prepared by solvent casting technique. Different ZnO percentages were used (1, 2, 3 and 4%). The EVA/ZnO composites were characterized using x-ray diffraction and scanning electron microscope (SEM) techniques. The mechanical properties were studied by both ultrasonic measurements and a tensile testing machine. By TGA, thermal properties of EVA/ZnO composites were determined. The piezoelectric properties of films investigated. To evaluate the films as piezoelectric material: acoustic impedance, frequency, sensitivity, ultrasonic attenuation coefficient and quality factor measured. The results deduced that the most suitable composite was EVA/ZnO 3%; It almost met the criteria of the highly sensitive ultrasonic transducer of high frequency. In addition, the prepared films of different ZnO concentrations could operate under high temperatures. Therefore, they could be used in high-temperature transducers.

1. Introduction
Piezoelectric materials are very important materials that used in many fields. Piezoelectric elements and materials are successfully used in smart systems as active sensors [1]. Different studies extend the use of piezoelectric materials alongside nanomaterials in numerous fields of application [2]. Recently, there has been big interest in piezoelectric energy harvesting (i.e., energy storing from external sources) [3]. Moreover, piezoelectric materials could be also the active elements of ultrasonic transducers. They receive the electrical pulse then vibrate to generate mechanical ultrasonic waves [4]. They could be made from many materials such as ceramic, polymer, ceramic-polymer composites [5], polymer-metal composites, etc. [6, 7]. Ceramic piezoelectric material is the most usable, but polymer piezoelectric materials compete them because of their advantage properties like mechanical flexibility; although ceramic-polymer piezoelectric materials combine the advantages of both ceramic and polymer materials [8, 9]. Many studies insured that piezoelectric polymer materials may offer highly sensitive transducers or broadband transducers that are suitable for many purposes. They may incorporate smart electro-active materials that have many industrial applications [10]. The most reputable piezoelectric polymer materials are poly (vinylidene fluoride) (PVDF) materials [11].

In some industrial applications, high temperature transducer is required to bear high temperature during operation like testing tanks or tubes that may contain hot chemicals, fuel, oil, etc. Some active elements can support high temperature and, in some cases, additive materials needed to lower the temperature of the surrounding of the transducer [12].

During the last years, polymer matrix composites (PMCs) having metals studied to act as very competitive active elements. They are flexible, soft, cheap, easy to prepare and they had good mechanical and electric properties. Therefore, they may be more suitable for some applications over ceramic materials. Flexible and soft PMCs used in medical transducers, tactile sensors, etc. Thus, many researchers interested in the design and fabrication of PMCs to make polymeric piezoelectric composites [13]. Polymeric piezoelectric composites composed of two essential components; polymer matrix and active piezoelectric granules, which may be metal
or metal oxide. From the point of view that poly (ethylene-co-vinyl acetate) (EVA) had low modulus, high flexibility, low temperature toughness, crack resistance and cheap, it used in cables, wires and flexible packaging. In addition, it may play the polymer matrix role in the preparation of polymeric piezoelectric composites [14].

Among the metal oxides, ZnO had many attractive properties to be used as the piezoelectric granules in the polymeric piezoelectric composites. Generally, ZnO is a semiconductor with a wide bandgap of about 3.33 eV. It had a high crystalline structure, high piezoelectric coefficient, high electromechanical coupling coefficients, low cost and good charge caring. Therefore, it had been successfully used in thin film piezoelectric devices [15].

Taking the advantage of both EVA polymer and ZnO, the main aim of this study was to prepare highly sensitive piezoelectric polymer films for ultrasonic transducers’ fabrication especially that used in fabrication of medical transducer and in high temperature transducer.

2. Materials and experimental methodology

2.1. Materials
Elvax 670 Ethylene-co-vinyl acetate (EVA) copolymer used for the preparation of composites was obtained from DuPont Packaging and Industrial Polymers (Wilmington, Delaware U.S.A.). The vinyl acetate content of the copolymer used was 12 wt% (Density is 0.933 g cm\(^{-3}\), Melt Flow Index was 0.35 g/10 min @190 °C). ZnO, and toluene were procured from Elnasr Pharmaceutical Chemical Co., Egypt.

2.2. Synthesis of EVA/ZnO composites films
Five grams of EVA was dissolved in 100 ml of toluene by heating at 45 °C for 16 h under mechanical stirring for the complete dissolution. 1% by weight of ZnO particles was added to the EVA solution with continuous heating for 30 min at 45 °C under stirring mechanically. EVA/ZnO solution sonicated for 30 min by the direct probe sonication method using a sonicator (Model FB 505, Fisher Scientific Co., Germany). The solution film was made in a glass petri dish with a diameter of 20 cm using a solvent casting technique and was dried at room temperature for 2 days, then for 2 h at 45 °C in an oscillating air oven. The thickness of the EVA/ZnO films was measured with a digital micrometer and found to be 0.1 mm. All the dried films were stored in a moisture-controlled desiccator for further testing and thus an EVA composite film with 1% ZnO was prepared. Similarly, EVA composite films for 2%, 3% and 4% of ZnO were prepared [16], figure 1 shows photos of EVA/ZnO composites.

The formulation used in the EVA/ZnO composites preparation is given in table 1.

2.3. XRD measurements
The x-ray diffraction (XRD) system was utilized to identify the obtained phases. It was done on an x-ray diffractometer (analytical-Emparyean, Cu k\(\alpha\)1 radiation, \(\lambda = 1.5404 \) Å, 40 kV, 40 mA, Netherlands). The data
The neat EVA composite exhibited two diffraction peaks centered at 2θ = 21.49° and 23.62°, which corresponded to the lattice planes 110 and 200, respectively, which were associated with the orthorhombic crystal phase of polyethylene. Below these angles, there is a wide halo which is due to the amorphous segments of EVA, as observed in figure 2(A) [23, 24].

Figures 2(B)–(E) showed the appearance of sharp and intense peaks, which indicated the crystalline nature of the ZnO particles. The characteristic diffraction peaks appearing at 2θ = 31.62°, 34.28°, 36.11°, 47.37°, 56.46°, 62.76°, 66.28°, 67.83° and 68.98° can be assigned to the crystallographic planes (110), (002), (101), (102), (110), (1103), (200), (112), and (201) respectively [25]. The highest peak intensity for 100 and 101 crystallographic plane is found in Figures 2(D) of the EVA/ZnO 3% composite. This may be due to the difference in the crystal structure in the EVA/ZnO 3% composite, as well as the presence of a high percentage of the tetragonal phase in the EVA/ZnO 3% composite in comparison with the other EVA/ZnO composites. This note was assured in table 3.

### Table 1. Formulation of EVA/ZnO composites.

| Composites       | Amount of EVA, gm | Amount of ZnO, gm |
|------------------|-------------------|-------------------|
| Neat EVA         | 5                 | 0                 |
| EVA/ZnO 1%       | 5                 | 0.05              |
| EVA/ZnO 2%       | 5                 | 0.10              |
| EVA/ZnO 3%       | 5                 | 0.15              |
| EVA/ZnO 4%       | 5                 | 0.2               |

2.4. Scanning electron microscopy (SEM)

The morphology of the EVA composites was studied by using a scanning Electron Microscope Instrument (Carl ZEISS Sigma 500 VP, coupled with EDS). The specimens of EVA composites were coated with 2 nm gold using a Leica EM ACE200 coating system [18].

2.5. Mechanical properties

The mechanical properties of the films were determined by the tensile testing machine and by ultrasonic measurements. The tensile Strength (MPa) and Elongation at maximum (%) measured on strip specimens with an overall length of 100 mm and a gauge length of 50 mm according to ASTM D882–18 by using a universal Testing Machine (Zwick Z010, Germany), with a load cell of 100 N at a 500 mm min^{-1} rate of separation. The results reported are the averages of five sub specimens of each EVA/ZnO composite [19]. Ultrasonic velocities (longitudinal, C_L and shear, C_S) and density (ρ) measured for the prepared EVA/ZnO films. Then the elastic moduli, Poisson’s ratio, Lamé constants and micro-hardness were calculated [20].

2.6. Thermogravimetry analysis (TGA)

Thermogravimetry Analyzer, a Perkin Elmer TGA7 apparatus (USA), was used to analyze the EVA composites in an N_2 atmosphere; temperature range from 30 °C to 700 °C; heating rate of 10 °C min^{-1} [21].

2.7. Piezoelectric constant measurements

The piezoelectric constant (d_{33}) values of EVA/ZnO composites were measured by the Piezo d_{33} Test System, Model YE2730 d_{33} [22].

2.8. Ultrasonic measurements

The ultrasonic mode of operation was the direct contact pulse echo technique using a single ultrasonic transducer, which acted as both a receiver and a transmitter of echoes. A longitudinal normal beam ultrasonic transducer of 4 MHz (S12HB4, Karl Deutsch) and a shear ultrasonic transducer of 2 MHz (S12Y2, Karl Deutsch) were used. The echoes were displayed on the CRT screen of the flaw detector (USN60, GE inspection technologies) and the time of flight of the echoes was determined by using an oscilloscope (LeCroy W, wave Jet 354A). Standards blocks (VI and VII) were used as reference test blocks to calibrate thickness measurements.

3. Results and discussion

3.1. XRD measurements

The neat EVA composite exhibited two diffraction peaks centered at 2θ = 21.49° and 23.62°, which corresponded to the lattice planes 110 and 200, respectively, which were associated with the orthorhombic crystal phase of polyethylene.
The addition of ZnO affected EVA lattice peaks; 1% and 2% of ZnO decreased the height of EVA lattice peaks may be due to the difference in the crystal structure of EVA composites as shown in table 3 [26]. From table 2, there was a slight upper shift in the 2θ position of signals in the EVA/ZnO 2% composite XRD pattern, while the 2θ position of signals in the EVA/ZnO 1%, 3%, and 4% composite XRD patterns slightly downshifted compare to the neat EVA composite film. The interplanar spacing (d-spacing) of signals in the EVA/ZnO 2% composite XRD pattern slightly down shifts while the d-spacing of signals in the EVA/ZnO 1%, 3%, and 4% composites XRD pattern slightly upper shifts compare to the neat EVA composite. This might indicate the alteration in the arrangement of the polymer chains with increasing ZnO content. Change in interlayer spacing indicated the change of ZnO content disturbed EVA composite crystallization and intercalation of ZnO particles into EVA composites [27].

The geometrical characteristics of ZnO in EVA/ZnO composites were calculated as reported in table 3, and evidence that the geometrical characteristics of ZnO changed with increasing the ZnO content in EVA/ZnO composites. The crystal structure of EVA/ZnO 1% was mainly amorphous in addition to a few hexagonal structures. EVA/ZnO 2%, 3%, and 4% had mainly amorphous structures, but ZnO caused the presence of a few orthorhombic crystal structures. The tetragonal crystal structure was present in both the EVA/ZnO 3% and EVA/ZnO 4% composites, but in much lower percentages than the amorphous one. We could estimate that both EVA/ZnO 3% and EVA/ZnO 4% composites will have characteristic piezoelectric properties because of

![Figure 2. X-ray diffraction patterns of (A) Neat EVA composite, (B) EVA/ZnO 1% composite, (C) EVA/ZnO 2% composite, (D) EVA/ZnO 3% composite, and (E) EVA/ZnO 4% composite.](image)
Table 2. Main signals in XRD patterns $2\theta$ (°), Height (cts), full width at half maximum (FWHM (°)), and d-spacing (Å) of EVA composites.

| Composites       | $2\theta$ (°) | Height (cts) | FWHM (°) | d-spacing (Å) |
|------------------|---------------|--------------|----------|---------------|
| Neat EVA         | 21.5          | 3286.1       | 0.31     | 4.142         |
|                  | 23.7          | 518.9        | 0.51     | 3.737         |
| EVA/ZnO 1%       | 21.37         | 2923.10      | 0.23     | 4.154         |
|                  | 23.75         | 425.40       | 0.72     | 3.744         |
|                  | 31.90         | 566.22       | 0.08     | 2.803         |
|                  | 34.54         | 230.94       | 0.08     | 2.595         |
|                  | 36.37         | 749.45       | 0.06     | 2.468         |
|                  | 47.62         | 107.41       | 0.08     | 1.908         |
|                  | 56.79         | 222.63       | 0.10     | 1.623         |
|                  | 62.94         | 106.23       | 0.10     | 1.475         |
|                  | 66.60         | 22.73        | 0.31     | 1.403         |
|                  | 68.00         | 96.87        | 0.10     | 1.377         |
|                  | 69.16         | 46.79        | 0.10     | 1.357         |
| EVA/ZnO 2%       | 21.74         | 994.97       | 0.18     | 4.085         |
|                  | 23.96         | 170.30       | 0.82     | 3.710         |
|                  | 32.08         | 496.81       | 0.13     | 2.787         |
|                  | 34.71         | 204.65       | 0.06     | 2.582         |
|                  | 36.53         | 623.05       | 0.10     | 2.458         |
|                  | 47.08         | 108.96       | 0.08     | 1.901         |
|                  | 56.85         | 226.08       | 0.09     | 1.618         |
|                  | 63.08         | 95.10        | 0.10     | 1.473         |
|                  | 66.60         | 20.67        | 0.31     | 1.403         |
|                  | 68.22         | 114.30       | 0.05     | 1.374         |
|                  | 69.36         | 53.77        | 0.09     | 1.354         |
| EVA/ZnO 3%       | 21.31         | 2444.32      | 0.15     | 4.165         |
|                  | 23.26         | 349.27       | 0.61     | 3.763         |
|                  | 31.62         | 2098.17      | 0.13     | 2.827         |
|                  | 34.28         | 710.85       | 0.12     | 2.614         |
|                  | 36.11         | 2258.68      | 0.10     | 2.485         |
|                  | 47.37         | 318.49       | 0.08     | 1.917         |
|                  | 56.46         | 686.21       | 0.12     | 1.629         |
|                  | 62.76         | 331.74       | 0.11     | 1.479         |
|                  | 66.28         | 91.63        | 0.09     | 1.409         |
|                  | 67.83         | 296.61       | 0.11     | 1.381         |
|                  | 68.69         | 182.83       | 0.11     | 1.360         |
| EVA/ZnO 4%       | 21.30         | 2211.21      | 0.13     | 4.168         |
|                  | 23.63         | 338.74       | 0.72     | 3.761         |
|                  | 31.66         | 1181.35      | 0.09     | 2.824         |
|                  | 34.31         | 543.50       | 0.06     | 2.615         |
|                  | 36.15         | 1618.64      | 0.08     | 2.483         |
|                  | 47.44         | 242.44       | 0.08     | 1.915         |
|                  | 56.51         | 440.85       | 0.08     | 1.627         |
|                  | 62.76         | 222.56       | 0.08     | 1.479         |
|                  | 66.29         | 72.56        | 0.06     | 1.409         |
|                  | 67.87         | 229.50       | 0.09     | 1.380         |
|                  | 68.99         | 124.48       | 0.09     | 1.360         |

Table 3. Geometrical characteristics of prepared EVA composites.

| Composites       | Geometrical characteristics |
|------------------|----------------------------|
|                  | $\alpha$, $\beta$, and $\gamma$ |
| EVA/ZnO 1%       | $a = \beta = 90^\circ$, $\gamma = 120^\circ$ |
| EVA/ZnO 2%       | $a = \beta = \gamma = 90^\circ$ |
| EVA/ZnO 3%       | $a = \beta = \gamma = 90^\circ$ |
| EVA/ZnO 4%       | $a = \beta = \gamma = 90^\circ$ |
the appearance of a tetragonal crystal structure, which is the most suitable crystal structure for atom resonance to acquire piezoelectric properties [28].

The major crystal structure of the prepared composites was amorphous as per the large area under curve in XRD figures (figure 2). This was due to the small percentage of ZnO (table 1), which was responsible for the fair appearance of hexagonal, orthorhombic, and tetragonal crystal structures.

3.2. Characterization of EVA composites by SEM

SEM images were used to qualitatively investigate the dispersion of ZnO particles within the EVA matrix and measure the particle size of the dispersed phase. Figure 3 showed ZnO particles were homogeneously dispersed in each EVA matrix without any obvious sign of aggregation in the case of EVA/ZnO 1% and EVA/ZnO 3% composites, and there was some simple aggregation in the case of the EVA/ZnO 4% composite. In addition, the evaporation of the solvent did not cause the formation of pores on the material surface, preserving a flat topography [29]. The average particle size of ZnO was 440.65 nm.

Figure 4 showed the EDX result of EVA composites. The neat EVA composite contained C and O elements. EVA/ZnO composites contained Zn element in addition to C and O elements. EVA/ZnO composites contained approximately the same amount of carbon as neat EVA composite. They contained a higher amount of oxygen and Zn elements, with an increase in the amount of ZnO in EVA composites.

3.3. Mechanical properties of EVA/ZnO composites

Tensile strength and elongation at a maximum are important properties of EVA composites that reflect the capability of EVA composites to be used in different applications.

The tensile strength of the neat EVA/ZnO composite was 6.2 MPa, figure 5. 1%, 2%, 3% and 4% of ZnO enhanced the tensile strength of EVA/ZnO composites by 20.4%, 56.9%, 96.5%, and 44.2% respectively compared to the neat EVA composite, figure 5. The addition of 3% ZnO leads to a significant improvement in
the tensile strength of the EVA/ZnO composite. ZnO particles tie up the EVA molecules to resist tensile deformations. Further increase in ZnO, reduced the tensile strength of the EVA/ZnO 4% composite [27]. The elongation at the maximum of the neat EVA composite was 1200%. The introduction of 1%, 2%, 3%, and 4% of ZnO fillers caused a slight decrease in the elongation at the maximum of the EVA/ZnO composites, figure 5. ZnO particles reduced the capability of EVA/ZnO composites to elongate [30].
Ultrasonic measurements were used to complete the mechanical properties characterization of the prepared EVA/ZnO composites. The crystal structure of the prepared composites was regarded as an amorphous structure, because the ZnO content was very small (1%, 2%, 3% and 4%), there was a homogeneous distribution of the ZnO particles in the EVA matrix as shown in SEM photos without aggregation (figure 3), and the amorphous structure was dominant as appeared in XRD figures (figure 2). Ultrasonic velocities (Longitudinal, $C_L$ and shear, $C_S$), determined $[31]$.

$$ C = \frac{2x}{t} \quad (1) $$

Where: $C$ is the ultrasonic velocity, $x$ is the thickness of the specimen and $t$ is the time travelled by the echoes.

Both longitudinal and shear velocities exhibited increments until reaching their maximum in the EVA/ZnO 3% composite, then decreased in the EVA/ZnO 4% composite, figure 6. The ZnO content inside the EVA matrix filled perfectly gaps and enhanced waves travelling, but further ZnO increment disturbed waves travelling and caused velocity decrement. Poisson’s ratio ($\nu$), elastic moduli ($E$, $L$, $G$, $K$), micro-hardness ($H$) and Lamé constants ($\mu$, $\lambda$) were calculated as following $[19, 32]$.

$$ \nu = \frac{1 - 2(C_S / C_L)^2}{2 - 2(C_S / C_L)^2} \quad (2) $$

$$ E = 2\rho(C_S)^2(1 + \nu) \quad (3) $$

$$ L = \rho(C_L)^2 \quad (4) $$

$$ G = \rho(C_S)^2 \quad (5) $$

$$ K = L - [(4/3)G] \quad (6) $$

$$ H = [(1 - 2\nu)E / (6(1 + \nu))] \quad (7) $$

$$ \mu = C_S^2 \rho \quad (8) $$

$$ \lambda = (C_L^2 \rho) - (2\mu) \quad (9) $$

Where: $\rho$ is the films density, $E$ is the Young’s modulus, $L$ is the longitudinal modulus, $G$ is the shear modulus and $K$ is the bulk modulus.

From figure 7(A), there was a slight decrement in Poisson’s ratio until reaching its minimum value for the EVA/ZnO 3% composite, then it increased by a small amount in the EVA/ZnO 4% composite. Whereas, Poisson’s ratio ($\nu$) could be affected by the changes in the molecular chain network; ZnO changed the bond strength of the molecular chain network of the composites, but without deterioration of the molecular chain network $[33]$.

In figure 7(B), the elastic moduli (longitudinal $L$, shear $G$, bulk $K$, and Young’s $E$) increased to their maximum for the EVA/ZnO 3% composite, then decreased for the EVA/ZnO 4% composite. Generally, they offer information about the material’s rigidity, intermolecular bond forces, etc. Thus, the EVA/ZnO 3% composite had the most well-arranged atoms in high flexible molecular chains $[31]$.

Figure 7(C) showed the same pattern of increment and decrement as figure 5(B). Micro-hardness ($H$) characterized the bond strength between atoms in the EVA/ZnO specimens $[34]$. The EVA/ZnO 3% composite had the highest bond strength between ZnO particles and the EVA matrix.
The Lamé constants ($\mu$, $\lambda$) increased as ZnO content increased; they were high in the EVA/ZnO 3% composite, figure 7(D). This may be due to the stress strain relationship between atoms in EVA/ZnO specimens [35]. ZnO 3% was the most adequate concentration that caused good incorporation into the EVA matrix.

### 3.4. Piezoelectric properties of EVA/ZnO composites

Piezoelectricity means the ability of a piezoelectric material to generate charges on its surface (i.e. internal electric field) when subjected to mechanical stress (direct piezoelectricity) or even to electric current (converse piezoelectricity) [36]. To demonstrate EVA/ZnO piezoelectric properties, the piezoelectric constant ($d_{33}$), the relative permittivity $\varepsilon_{33}$ and the piezoelectric voltage constant, $g_{33}$ were studied.

Generally, the piezoelectric constant ($d_i$) is the polarization generated per unit of mechanical stress applied to a piezoelectric material. The first subscript ($i$) to $d$ indicates the direction of polarization generated in the piezoelectric material when the electric field is zero. The second subscript ($j$) is the direction of the applied stress. Thus, $d_{33}$ is the polarization, which induces piezoelectricity in direction 3 [35].

From figure 8(A), it has been found that the incorporation of ZnO particles substantially enhanced the piezoelectric coefficient ($d_{33}$) of the EVA/ZnO composites. With 1%, 2%, 3%, and 4% loading of ZnO filler, the $d_{33}$ has been observed to increase by 77.8%, 116.7%, 139.7%, and 99.2% compared to the neat EVA composite, respectively. $d_{33}$ reached the maximum at 3% ZnO concentration, thus the EVA/ZnO 3% composite acquired good piezoelectric properties over the other prepared composites. This may be due to the presence of a tetragonal crystal shape as the major shape in this composite and its high mechanical properties as previously mentioned [37].

Piezoelectric coefficient is a function of composition and crystal orientation [38]. Therefore, we can say that the prepared EVA/ZnO composites were mainly amorphous but they still had some other crystals structures like hexagonal, tetragonal and orthorhombic due to ZnO incorporation in EVA matrix. These composites had very low piezoelectric coefficient, figure 8(A), compared to other materials like PZT, PMN-PT, etc.

The relative permittivity is the permittivity of a given material relative to that of the permittivity of a vacuum. It indicates the ability of the material to store energy from the applied electric field.

$$\varepsilon_{33} = \frac{TC}{\varepsilon_0 S} \quad (10)$$
Where, $\varepsilon_{33}$ is the relative dielectric constant or relative permittivity, $T$ is the thickness of test specimen (m), $S$ is the area of sample electrode ($m^2$), $C$ is the capacitance of test specimen (F), and the absolute permittivity $\varepsilon_0$ is the permittivity of free space that equal to approximately $8.85 \times 10^{-12}$ Farads/m [39].

We observed that 1%, 2% and 3% EVA/ZnO composites had nearly equal values of the relative permittivity, while the neat EVA composite had the highest value and the 4% EVA/ZnO composite had the lowest value of the relative permittivity, figure 8(B). The incorporation of ZnO affected the crystal structure of the prepared composites, therefore changing the ability of the composite to store energy from the applied electric field [36].

The piezoelectric voltage constant, $g_{33}$ is the electric field generated by a piezoelectric material per unit of applied mechanical stress. It induced an electric field in direction 3 (parallel to the direction in which a piezoelectric element is polarized) per unit stress applied in direction 3. It is important for assessing a material’s suitability for sensor applications because the strength of the induced electric field produced by a piezoelectric material in response to applied physical stress is the product of the value of the applied stress and the value of $g_{33}$.

$$g_{33} = \frac{d_{33}}{\varepsilon_{33}}$$ (11)

Figure 8(C) represented the piezoelectric voltage constant ($g_{33}$) as a function of EVA/ZnO composites. The piezoelectric voltage constant increased with the increase in the content of ZnO from 0 to 4% and the highest value was at 3% ZnO. From all determined piezoelectric properties, we deduced that the piezoelectric response of EVA/ZnO composites improved with increasing the content of ZnO, and 3% of ZnO is the best for piezoelectric applications, whereas this content of ZnO improves piezoelectric coefficient and piezo voltage constant by 139.7% and 150% compared to that of the neat EVA/ZnO composite [36].

### 3.5. Thermal stability

The TGA and DrTGA curves show a comparison of the thermal stabilities of neat EVA, EVA/ZnO 1%, EVA/ZnO 2%, EVA/ZnO 3% and EVA/ZnO 4% composites, figures 9(A) and (B). Table 4 summarizes the initial ($T_{\text{initial}}$), final ($T_{\text{final}}$) and maximum ($T_{\text{max}}$) temperatures, and weight loss % and ash residue % of these composites.

Thermograms of EVA composites illustrated the degradation process that occurred in two steps, as shown in figure 9 and table 4. The first weight loss started at 220 °C for the neat EVA composite, which extended up to 258 °C, 260 °C, 262 °C, and 263 °C for the EVA/ZnO 1%, EVA/ZnO 2%, EVA/ZnO 3%, and EVA/ZnO 4%
composites respectively. It referred to the loss of acetate. The second weight loss started at 360 °C and referred to the degradation of the C–C and C–H bonds of ethylene. The 3% of ZnO improved the thermal stability of the EVA/ZnO composite during the first weight loss where the value of the initial decomposition temperature \( T_{\text{initial}} \), the temperature at 10% degradation \( T_{10\%} \) and the temperature at maximum degradation rate \( T_{\text{max}} \) increased by 43 °C, 7 °C and 2.7 °C respectively in comparison with the neat EVA composite. The ash residue % of the EVA/ZnO 3% composite is 5.7% due to the interactions between ZnO particles and the polymer matrix [36].

3.6. EVA/ZnO composites application

In addition to the above measurements of the prepared EVA/ZnO composites; we could summarize some important features that demonstrated the usefulness of the prepared films in many applications, especially in medical ultrasonic transducer manufacture, and in high temperature transducer manufacture.

1. The prepared EVA/ZnO films had low acoustic impedance \( Z \) compared to those of ceramic piezoelectric materials. Their acoustic impedance varied from 1.2 to 2.7 that of water \( (Z_{\text{water}} = 1.48 \text{MPa}) \), so they can be used easily in ultrasonic medical diagnosis, because their acoustic impedance was matched close to tissues, table 5. A close impedance match permits more efficient transduction of acoustic signals in water and tissue [40].
2. EVA/ZnO films had high sensitivity (S). Piezoelectric material sensitivity (S) is an important factor that determines the ability of the transducer to detect different defects. It is the relationship between the voltage applied to the transducer, $V_o$, to that received from the load specimen, $V_x$:

$$S(dB) = 20 \log \left( \frac{V_x}{V_o} \right)$$  \hspace{1cm} (12)

It was found that EVA/ZnO films can be directly attached to a structure without disturbing its mechanical motion. Therefore, they had high sensitivity as appeared in table 5. EVA/ZnO 3% had the highest sensitivity value.

3. EVA/ZnO films had a high-quality factor (Q). The Piezoelectric material’s quality factor, Q, is the description of the amount of ringing and damping of the material. It is the operating frequency, $f_o$, divided by the bandwidth, BW:

$$Q = \frac{f_o}{BW}$$  \hspace{1cm} (13)

Q factor was calculated according to the spectrum chart picked by the vector signal analyzer, which indicated a $-6$dB drop, the lower frequency ($f_l$) and upper frequency ($f_u$). The bandwidth (BW) and the central (operating) frequency ($f_o$) were calculated according to the following [23, 24]:

$$f_o = (f_u f_l)^{1/2}$$  \hspace{1cm} (14)

$$BW = (f_u - f_l)$$  \hspace{1cm} (15)

From table 5, EVA/ZnO 3% film had the highest value of quality factor; high Q factor piezoelectric material produced a relatively pure frequency spectrum and had a narrow bandwidth (i.e., light damping) with a corresponding long special pulse length (i.e., long ringing). This assures its usefulness in medical ultrasonic transducer fabrication.

4. The EVA/ZnO films had a high frequency in the range of 25 MHz, and their bandwidth ranged from 0.2 to 0.6 MHz, table 5. Therefore, they had high acoustic energy transfer in medium, especially tissue and water.

5. EVA/ZnO films could be prepared in a wide thickness range; they were malleable, soft, elastic and easy to couple on the surface. In addition, they were stable to change as deduced from ultrasonic attenuation coefficient ($\alpha$) measurement, figure 10. The variation in ultrasonic attenuation coefficient was not great for 2%, 3% and 4% EVA composites. That means high stability. Generally, ultrasonic attenuation coefficient ($\alpha$) picks up any variation in the material as a result of any chemical or physical change. It was measured by comparing the amplitudes of the pulses (l) that travelled different acoustic paths (x) in the specimen under study according to the following equation [29]:

$$\alpha = ((1/(x_x - x_i))(\ln (l_1/l_2)$$  \hspace{1cm} (16)
As per two successive echoes height measurements, the ultrasonic attenuation coefficient ($\alpha$) was measured in dB/cm.

6. EVA/ZnO films had high thermal stability and could bear high temperatures, so they may be useful in high temperature transducer fabrication [39].

4. Conclusion

EVA/ZnO films prepared by the solvent casting technique. They had an attractive crystal structure to be used as a piezoelectric material, XRD demonstrated that there were mostly orthorhombic and tetragonal crystal shapes. They had good mechanical properties, high thermal stability, and good piezoelectric properties. They had excellent characteristics to be applied in many applications that serve ultrasonic transducer fabrication (medical transducers, high temperature transducers, etc.). Moreover, they had a high capability to detect defects in different structures. They had a high frequency (about 25 MHz), low acoustic impedance, high quality factor, high sensitivity and high stability to change. In addition, the prepared composites were films, which were malleable, soft, elastic, and easy to couple on the surface. Among the prepared films, EVA/ZnO 3% exhibited very useful properties.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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