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Research paper

Fabrication and Characterization of Piezoelectric Polymer Nano Composites for Humidity Sensors Applications

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Abstract

Piezoelectric polymer nano compositesfor humidity sensors applications are manufactured in this work by adding nano Yttrium oxides (Y_2O_3) in three ratios (3,6and 9 wt.%) to the polymeric blend consist of (1:9) poly vinyl difluoride (PVDF) and poly methyl methacrylate (PMMA). FTIR results showed that PVDF addition to PMMA causes shifting in the blue direction and there is no chemical bonding between the prepared composites components,butthere is a significant increase in the rate of permeabilityat higherY_2O_3 ratio. This addition causes the hardness to be increased linearly. Morphology results showed, that the lower ratios of Y_2O_3 causes the surface became smoother and homogeneous, while higher ratios increase the roughness of the surface. These compositesgive piezoelectric behavior where the electrical resistance decreases by increasing the pressure. With regard to the dielectric properties the losses coefficient increase by increasing the frequency while dielectric constant decreases. The composites showed to be more hydrophilic by increasing theY_2O_3 ratio,which suggests these composites for water storage applications. The results show possibility of using these composites as humidity sensorsin relative humidity less than 70%, where the electrical resistivity decreases as the relative humidity increasing.

Keywords: *Piezoelectric polyme Humidity sensor PVDF PMMA*

1. Introduction

Piezoelectricity is the electric charge that accumulates in certain solid materials (such as topaz, crystals, can sugar, certain ceramics, bone, DNA, various proteins and some polymers) in response to applied mechanical stress [1]. When these material are subjected to mechanical stress, this generates electric charge proportional to the applied stress. In contrast, piezoelectric materials can generate a mechanical strain when an electric field is applied to them [2]. These materials used in many applications, such as mobile phones, automotive electronics, medical technology, communication systems, defense, industrial automation, medical diagnostics [3], energy harvesting and industrial systems [4].

The important parameters for a piezoelectric material are piezoelectric charge constant, piezoelectric voltage constant and the dielectric constant [5].The piezoelectric charge constant reflects the polarization generated per unit mechanical stress applied to a piezoelectric material (or) the mechanical strain experienced by a piezoelectric material per unit of electric field applied [6].

The piezoelectric voltage constant is the electric field generated per unit applied stress by a piezoelectric material (or) the mechanical strain experienced by a piezoelectric material per unit electric displacement applied [7]. The dielectric constant is the ratio between the charge stored between a pair of electrode plates separated by a medium and the charge that can be stored under the same conditions by the same electrodes when separated by vacuum [8].

Humidity sensors are tools used to measure the humidity in terms of either absolute humidity, dew point or relative humidity (RH). Different types of these tools are available nowadays, such as those based on thermal conductivity, resistive and capacitive, which are highly durable,accurate and cost effective.In addition to humidity measurement, these tools can be used in various applications, such as weather stations, clothes dryers, leak detection, computer printers and incubators [9].

Choice of suitable type depends on many factors, such as accuracy, repeatability, contaminant resistance, stability and cost.

These sensors used different principles. Thermal conductivity type measures the difference between the thermal conductivity of dry air and air containing water vapor, while resistive type measures the impedance change.The concept of changing of the dielectric constant with humidity used in capacitive RH humid sensor with response time of half to one minute and temperature up to 200^oC [8].

Withlow hysteresis and quick response,thermoset polymer-based capacitive RHsensors can detect any changes in relative saturation as a change in sensor capacitance [9].

On comparison, with the thermoplastic-based capacitive sensors, thermoset type seems to be more efficient in resist liquids and vapors for many chemicals, such as toluene, oils and benzene. Furthermore, this type suitable for high temperatures and provides longest operating life.

Thin films of this type have ideal response to the relative humidity as shown in the following equation:

$G = R\ TLn\ (P/P_o)$

Where:G: driving forcefree energy for absorption, R: gas constant, T: sensor temperature, P: partial water vapor pressure and P_o: saturation water vapor pressure[10].

2. Experimental Part

Nano polymeric piezoelectric composites were prepared by adding 3%, 6% and 9wt% of nano Yttrium oxide (Y_2O_3) to the PVDF/PMMA (10/90) polymeric blend.
PMMA particles were mixed with different amounts ofnano Y_2O_3using magnetic stirrer for 1hr and 80°C in THF solvent, then PVDF powder was mixed for 1hr. The resulting paste was molded to obtain film with 1.5 mm thickness.
Piezoelectricity test was carried out using the Keithley 2440 Source Meter.SL200B Optical Dynamic / Static Contact Angle Meter used to measure the wettability angle. IR Affinity-1 Shimadzu device usedto cheek the bond types which may arise among film components. Atomic Force Microscopy (AFM) and optical microscope were used to study the morphology of the prepared films. Dielectric properties of D.C and A.C where measured by HIOKI 3532-50 LCR Hi device tester. Hardness was measured by Shore D Scale, DSC techniques was used to study the temperature transformation. Investigation of using this composites as humidity sensors was done by measuring it's electrical resistivity in the wide range of relative humidity (10%-90%).

3. Results and discussions

FTIR results: Figure 1 shows the FTIR spectrum of PVDF, PMMA and their (10/90) blend. For PVDF spectra, peaks at 840 and 880 belong to C-F stretching and C-C-C asymmetrical stretching vibration respectively. Peak at 1185 cm^{-1} belong to the C-C band. Peak at 1404 cm^{-1}refers to the wagging vibration mode of CH_2. Peaks at 2980 cm^{-1} and 3022 cm^{-1} belongs to symmetric and asymmetric vibrations of CH_2 [11]. Peaks at 533 $cm^{-1}$and at 1070 cm^{-1} belong to CF_2 bending and C-C stretching respectively. For PMMA spectra, peck at 3437 cm^{-1} belongs to –OH stretching.
It is clear that after the addition of PVDF to the PMMA, there is a decrease in intensity by up to about 40%, so that the material became absorbent to the infrared radiation. There is a shifting at the 2940 cm^{-1}in the blue direction due to the decrease of the length of the material after the addition of the PVDF and due as well as to the low permeability after this addition. The PVDF atoms filled the voids in the PMMA membrane,which made it more homogeneous

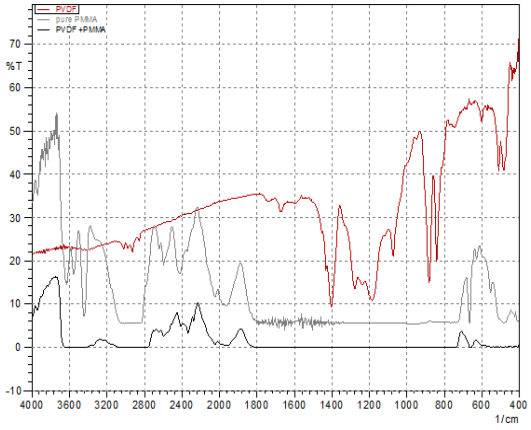

Fig. 1: FTIR spectrum of PVDF, PMMA and their blend

Figure 2 shows the FTIR spectrum of the neat blend and itsY_2O_3 composites. At 3 wt%, the intensity is the least possible because the ratio is very low. This addition does not affect the structure. Therefore, the permeability and crystalline structure are not affected. At 9wt% there is a significant increase in the rate of permeability compare with the neat blend in the (800-600 cm^{-1}) and (2700-2800 cm^{-1}) wave numbers.

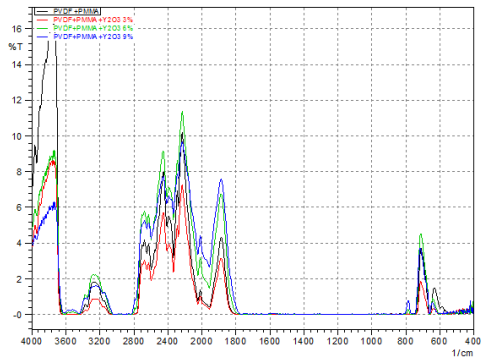

Fig. 2: FTIR spectrum of PVDF/ PMMA blend and its composites

Hardness results: Shore D hardness results showed that the hardness values for PMMA, PVDF and 90% PMMA / 10% PVDF blend are 71, 23 and 62 respectively. This means that the hardness of the blend dos not obey the mixture role and the blend is immiscible. Y_20_3 addition increases the hardness linearly as shown in figure 3. This is due to the high hardness of Y_20_3 itself.

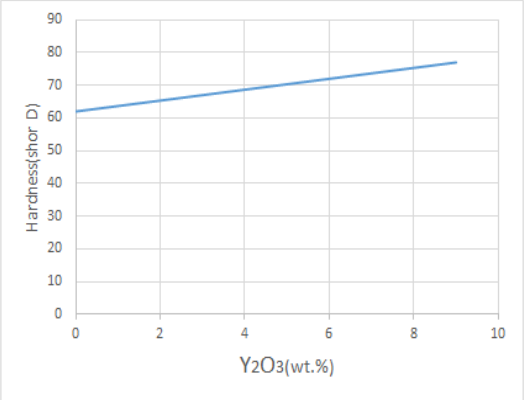

Fig. 3: Effect of Y_20_3 on the hardness

Morphology results: Figure 4 shows the optical microscopy images for pure blend and 3wt% and 9 wt% of its composites. It is clear that, the first addition (3wt%) causes the surface to be smoother and more homogenous, while the last addition (9 wt%) increases the roughness.
This is due, that small amount of Y_2O_3 filler occupy voids among blend molecules, while high concentration causes accumulation of filler particles at certain positions.

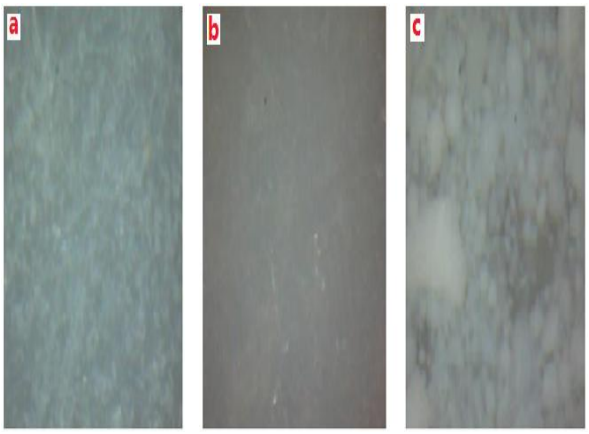

Fig. 4: Optical microscopy images for a- neat blend b- 3 wt% composite c- 9 wt% composite

These results coincide with AFM results as shown in figures 5 and 6 (2D and 3D respectively), were S_a and R_a roughness parameters increased for last addition.

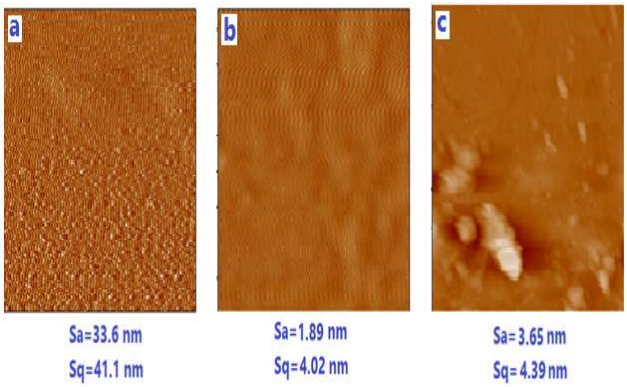

Fig. 5: 2D AFM images of a- neat blendb- 3 wt% composite c- 9 wt% composite

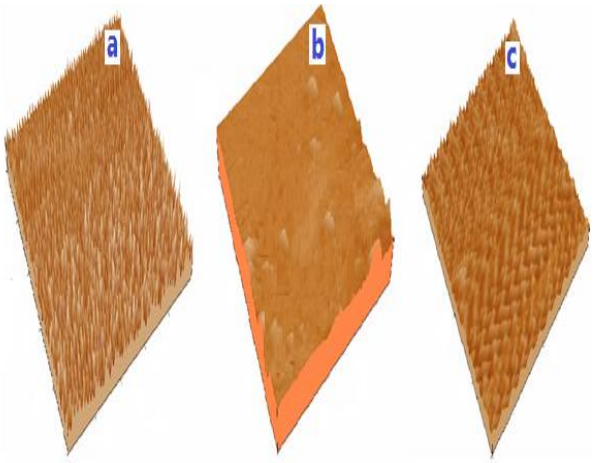

Fig. 6: 3D AFM images of a- neat blendb- 3 wt% composite c- 9 wt% composite

Piezoelectricity results: Figure 7 shows the relationshipbetween the electrical resistance and the applied pressure for the prepared samples. It is clear that, the resistivity of samples are pressure function, which indicates the piezoelectricity nature of theses samples and at the higher ratio, as pressure increases, the resistivity decreased. Also, it is clear that the resistance increased as Y_2O_3 content increased for a certain pressure. This is due to the filler nature; Y_2O_3 is an oxide material which is an insulator. Another reason is due to the fact that, when Y_2O_3nano particles occupy voids, this will leads to restrict the atomic vibration movements, which turn in increasing the resistance.

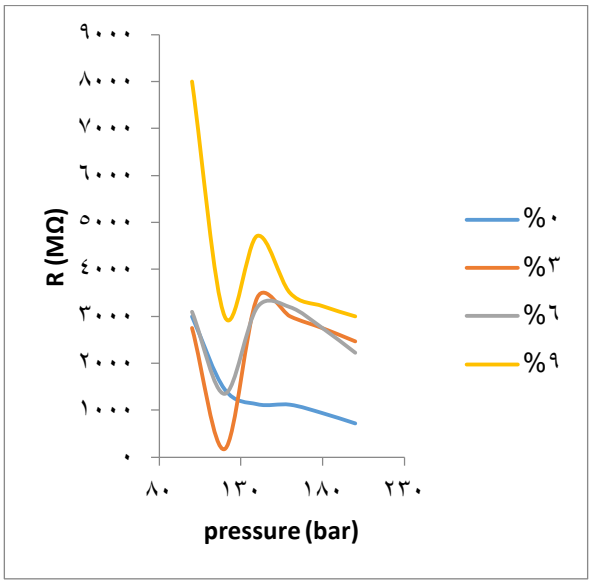

Fig. 7: The dependency resistance on pressure for the prepared samples

Generally, for each sample, as frequency increased, the losses (tan δ) increased as shown in Figure 8, while the dielectric constant dropped suddenly as the frequency increased (figure 9) and this reduction appear most obvious in high concentrations, which suggests that theY_2O_3 addition increases the forbidden gap.

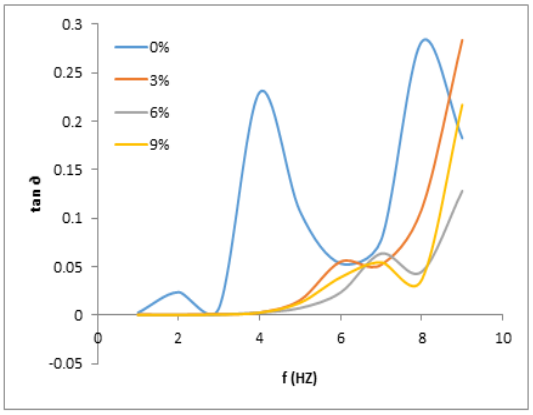

Fig. 8: Effect of frequency on losses factor

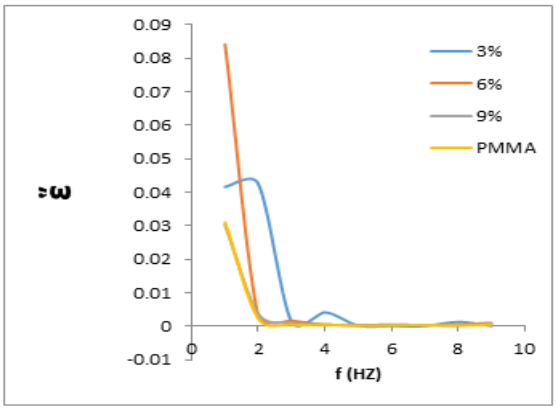

Fig. 9: Effect of frequency on dielectric constant

Wettability test: Table 1 shows the wettability results for 0% and 9% Y_2O_3samples.As the percent of Y_2O_3increased, the contact angle will decreasedfor different capture times and the blend become more hydrophilic. Also, it is clear that hydophilicity increased with time, which suggests these composites for water storage applications, such as membranes and agriculture water harvesting.

Table 1: Contact angles for 0% and 9%Y_2O_3samples

Capture time (min)	Y_20_3 (wt %)	
	0	9
0	59.65482	53.89345
2	57.26077	51.4066112
3	52.91916	50.52679

Humidity sensor results: Figure 10 shows the relationship between the electrical resistance and the relative humidity for 3wt% and 9wt% of nano Y_20_3 in the PVDF/PMMA blend.

Figure 10: Electrical resistivity as a function of relative humidity
It is clear that the electrical resistance decreases as the relative humidity increase for both samples. This is because that PVA and PVDF polymers due to their polar nature can attract to –OH group of water and decreases the resistance. As the prepared sample adsorbs humidity, the charges carriers concentration increased, which in turn increase the conductivity. The dissociation tendency of hydrogen ions, also increased as adsorption rate increased, which in turn accelerates the liberation of electrons and enhance the conductivity.
Also, it is clear that the span of sensitivity for 9wt% sample (from 184-205MW) is larger than 3wt% sample(from 175-195MW).

This figure shows also, that there is stability of the resistivity at high values of relative humidity (more than 70 RH %) which means that these polymeric composites don't respond to the variation of humidity at higher values which limits their uses as humidity sensor in relative humidity less than 70%.

4. Conclusions

The addition of Y203 causes no effect on the structure and the permeability of the PVDF/PMMA blend especially at ratios lower than 9% wt.
All sample exhibits the piezoelectricity effect; the electrical resistance decreased as the pressure increased.
The prepared samples can be used as a humidity sensors up to 70% RH; the electrical resistance decreased as the relative humidity increased.
The addition of Y203 make the samples more hydrophilic than the net blend and the hydophilicity increased with time, which suggests these composites for water storage applications.
The hardness of the resultant blend does not obey the mixture rule and increased linearly with the Y2O3 addition.
At low concentrations of Y203, the surface became smother and more homogenous compared with net blend, while high concentration (9wt%) the roughness increased.
For dialectical properties, the losses factor proportional inversely with the concentrations and the dielectrical constant dropped suddenly with the frequency.

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