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Effect of sulfonated poly (ether ether ketone) on the sensitivity of polyvinylidene fluoride-based resistive humidity sensors

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ABSTRACT

We have investigated the effect of sulfonated poly (ether ether ketone) (SPEEK) on the thermal stability, hydrophilicity, and sensitivity of polyvinylidene fluoride (PVDF) films based resistive humidity sensors. The blended film was deposited on the pre-patterned interdigited ITO glass electrode by the spin coating technique. The thermal stability of the PVDF-SPEEK composites investigated by thermogravimetric analysis. The surface morphology of the composite blend films has been studied by field emission scanning electron microscopy and atomic force microscopy analyses. The morphology of the PVDF-SPEEK blend films indicates that the PVDF-SPEEK blend is not uniform at high concentrations of SPEEK (over 10 wt%). The hydrophilicity of the sensing film studied by the contact angle method. As the concentration of SPEEK increases in the blend film, the hydrophilicity of the composite film also increases, which enhances the sensitivity of the sensing film. The impedance response of the PVDF-SPEEK blend film shows that the addition of SPEEK enhances the sensitivity of the sensing film at a lower humidity level. Moreover, the response and recovery times of the PVDF-SPEEK (2.5−5 wt%) are found to be 25 s and 65 s, respectively.

1. Introduction

Humidity sensors are applied extensively in industrial manufacturing, packing process, and quality control to monitor and detect the humidity level. Most of the corresponding research focuses on developing humidity sensors, which are highly sensitive, accurate in measurement, having fast response and recovery times, and showing stable and repeatable responses. In our previous study, we have studied the effect of TiO_2 and $BaTiO_3$ nanoparticles on the humidity sensing characteristics of PVDF based capacitive humidity sensors [1,2]. The fabricated capacitive humidity sensors exhibited low sensitivity at low relative humidity (below 40 %RH). The polymeric resistive humidity sensors showed significant improvements in terms of humidity sensors' sensitivity, simplicity, and integration with electronic circuits as compared to the capacitive humidity sensor [3,4]. Therefore, in this work, we aim to enhance the sensitivity of polymeric resistive sensors.

To improve the sensitivity of resistive humidity sensors, the essential property of the sensing film is its electrical conductivity and hydrophilicity. Different methods used to enhance the hydrophilicity and electrical conductivity of polymeric films. These methods include the grafting of the polymer [5], incorporation of hydrophilic nanoparticles within the polymeric chain [6], copolymerization of hydrophobic monomers [7], and blending of conductive polymers [8]. The addition of hydrophilic nanoparticles within the polymer may improve the hydrophilicity of the sensing film, which will increase the sensitivity of the humidity sensors. However, a higher concentration of nanoparticles leads to agglomeration, which will cause hysteresis losses in the humidity sensor. The blending of polymers, which have unique characteristics, is a well-known method to improve the mechanical and electrical properties of the sensing film [9].

Poly ether ether ketone (PEEK) is a high-performance polymer that has excellent mechanical properties, thermally stability, and chemical resistance [10,11]. The sulfonation of PEEK is a well-established method to improve the hydrophilicity and proton conductivity of the sensing film [12,13]. The sulfonation occurs by introducing the hydrophilic sulfonic groups (SO_3H) within the PEEK. The sulfonation of

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polymer significantly improves the adsorptions of water molecules and proton conductivity, which will increase the sensitivity of the humidity sensors [14]. Carretta et al. [15] prepared the sulfonated poly (styrene) (SPS); they observed that the casting of the sulfonic group improves the proton conductivity of the membrane. Rubinger et al. [16] fabricated resistive humidity sensors by depositing sulfonated poly (styrene) (SPS) on a ceramic substrate using the dip-coating method, and they reported a higher desorption time (around 5 min) as a result of sulfonation. Zhuang et al. [17] investigated the sulfonated poly (ether ether ketone) (SPEEK) based resistive humidity sensors, and they observed that the sulfonation degree plays a crucial role in improving the humidity sensitivity of the PEEK. Resistive humidity sensors based on hydrophilic polymers easily dissolved in water, as the sensors exposed to the high humidity level. Resistive sensor's accuracy and stability degrade with time, and sensors don't exhibit repeatable and stable response [18,19]. Therefore, to improve the stability and durability of resistive humidity sensors, we need to blend SPEEK with a polymer that is mechanically and thermally stable and improves the sensitivity of the humidity sensor.

Polyvinylidene fluoride (PVDF) is a hydrophobic polymer that has high thermal stability, excellent electrical properties, and high chemical resistance. Owing to these unique properties of PVDF, many researchers are investigating PVDF based sensing films for humidity sensing applications [20,21]. In this study, PVDF is blended with different concentrations of SPEEK to enhance the sensitivity of the resistive humidity sensor. We have studied morphology, thermal stability, and hydrophilicity of PVDF-SPEEK blend films. The films have been deposited on ITO/glass electrodes by the spin coating technique. Field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) is used to study the surface morphology of PVDF-SPEEK blend films. Thermal gravimetric analysis (TGA) is employed to analyze the thermal stabilities of the blended films. The electrical characteristics of the PVDF-SPEEK based resistive sensors studied in a controlled humidity chamber. The contact angle measurement is used to study the hydrophilicity of the sensing film. We have investigated different concentrations of SPEEK (1 wt%, 5 wt%,7.5 wt%, 10 wt%, and 15 wt%) on the morphology, hydrophilicity, and the electrical response of the PVDF-SPEEK based resistive sensors.

2. Experimental procedure

2.1. Materials

Sulfonated polyether ether ketone (fumion® E-590) with ion-exchange capacity (IEC) of 1.7 meq/g, was obtained from FuMA-Tech GmbH, Bietigheim-Bissingen, Germany. Polyvinylidene fluoride with an average Mw∼534,000 g/mol (by GPC) and N, N-dimethylacetamide (DMAC) purchased from Sigma Aldrich.

2.2. Preparation of PVDF-SPEEK blend solution

The PVDF-SPEEK blended solution prepared in a two-step process. First, the PVDF with a concentration of 2.5 wt% placed in the DMAC solvent. PVDF dissolves in DMAC solvent after 5 hrs of continuous magnetic stirring at 500 rpm. Different concentrations of SPEEK (1 wt%, 3 wt%, 5 wt%, 7.5 wt%, 10 wt%, and 15 wt%) were prepared separately in the DMAC solvent. To dissolve SPEEK completely in DMAC, it needs stirring at 500 rpm for 6 hrs. PVDF and SPEEK solutions in DMAC then mixed in a 1:2 volumetric proportion. The mixed solution was again stirred magnetically for 3 hrs to ensure thorough blending of the PVDF and SPEEK solutions. The fabrication process involved in this study is depicted in Fig. 1.

2.3. Fabrication and characterization

A spin coating technique is used to coat the PVDF-SPEEK blend solutions on the ITO/glass substrate (from Osilla). An optimization process is performed to optimize the rotation speed and the rotation time in order to form an even uniform film with the solutions. The optimum rotation speed and rotation time found to be 6000 rpm and 50 s, respectively. An optical contact angle device is used to measure the hydrophilicity of the blended film through the SCA software. The machine measures the angle of the water droplet on the surface of the film through a high definition camera lens. The lens can zoom to six times and can record 2450 frames per second. The morphological analyses necessary to determine the homogeneity and surface defects of the blended film conducted by the FESEM and AFM analysis. Whereas the X-

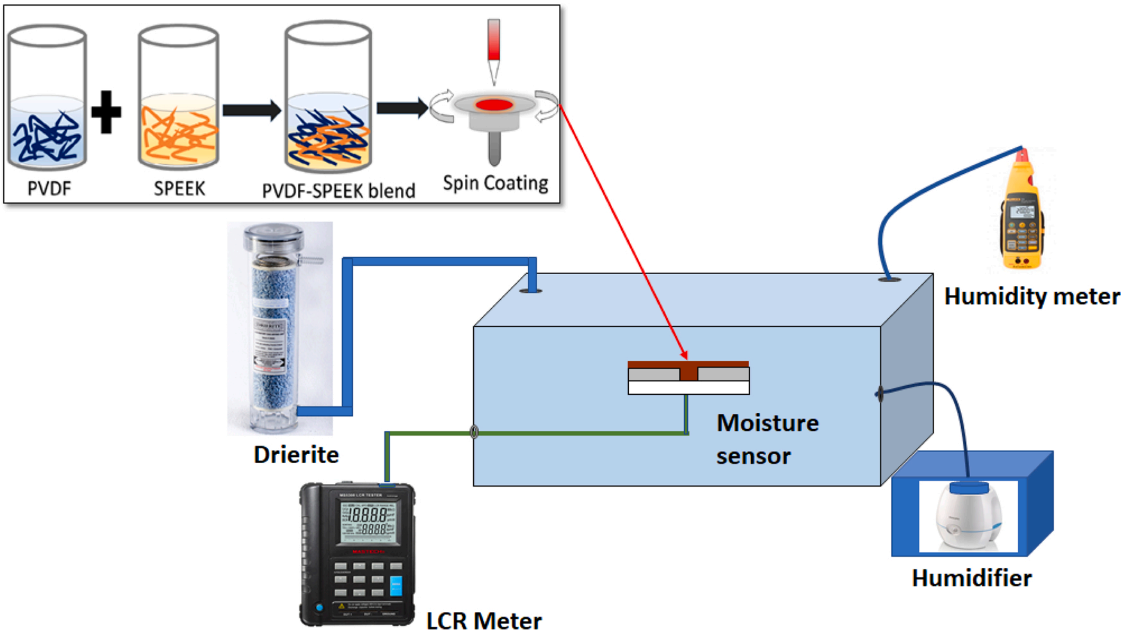


Fig. 1. Graphical presentation of the blending of PVDF and SPEEK solutions, deposition of the sensing film using the spin coating technique, and the humidity sensor experimental setup used in this work.

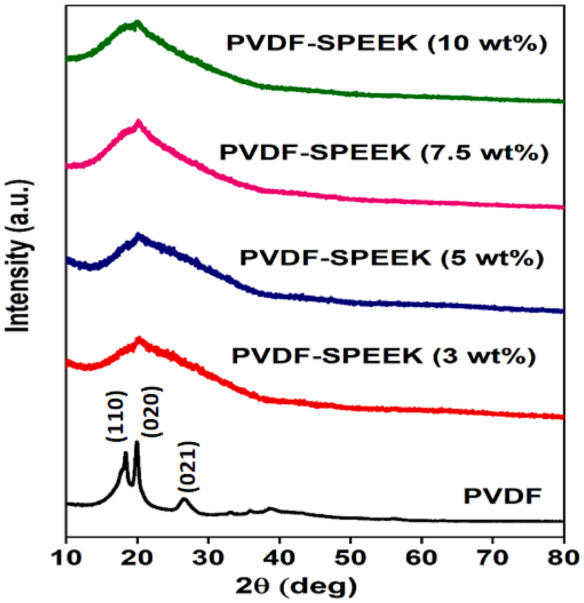


Fig. 2. XRD spectra of PVDF, PVDF-SPEEK (3 wt%, 5 wt%, 7.5 wt%, and 10 wt %) blend composites films, the concentration of PVDF in the blend films was fixed at 2.5 wt%.

ray diffraction (XRD) and thermogravimetric analysis (TGA) conducted to determine the interaction between PVDF and SPEEK within the blend films and thermal stability of the blended films. The electrical characterization of humidity sensors was carried out by our previously reported method [1].

3. Results and discussions

3.1. Structural analysis

X-ray diffraction analysis was performed to investigate the structural characteristics of the PVDF-SPEEK blend. Fig. 2 shows the XRD patterns of neat PVDF and PVDF/SPEEK blend composites. The peaks observed at 18.3°, 20.1°, and 26.6° correspond to the (110), (020) and (021) crystalline planes of pure PVDF [22]. It is observed that the peak at 18.3° is disappeared, and the peak at 20.1° is shifted to higher 2θ values when the SPEEK was incorporated in PVDF. The peaks were broadened with the increasing SPEEK contents, as shown in Fig. 2. No additional peaks observed in the composite, which suggests a strong interaction with the matrix of SPEEK and PVDF.

3.2. Morphological analysis

The morphology of the PVDF-SPEEK blend film determines the distribution of SPEEK within the blend film matrix. A morphological study of the PVDF-SPEEK blended film performed by FESEM and AFM analyses. Fig. 3 shows the SEM pictures of PVDF-SPEEK blend films with

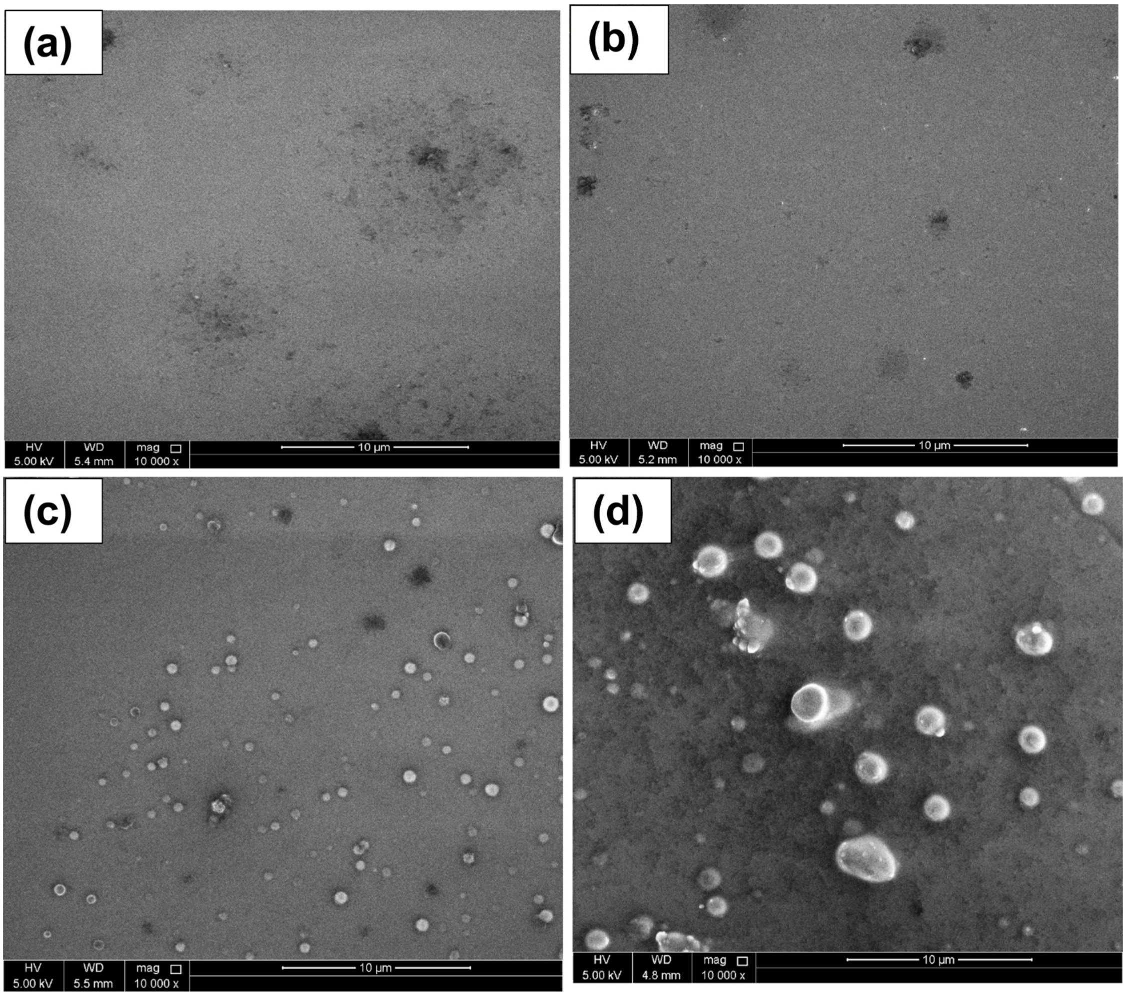


Fig. 3. FESEM micrographs of 2.5 wt% PVDF- SPEEK blend films with SPEEK concentrations of (a) 5 wt%, (b) 7.5 wt%, (c) 10 wt%, and (d) 15 wt%.

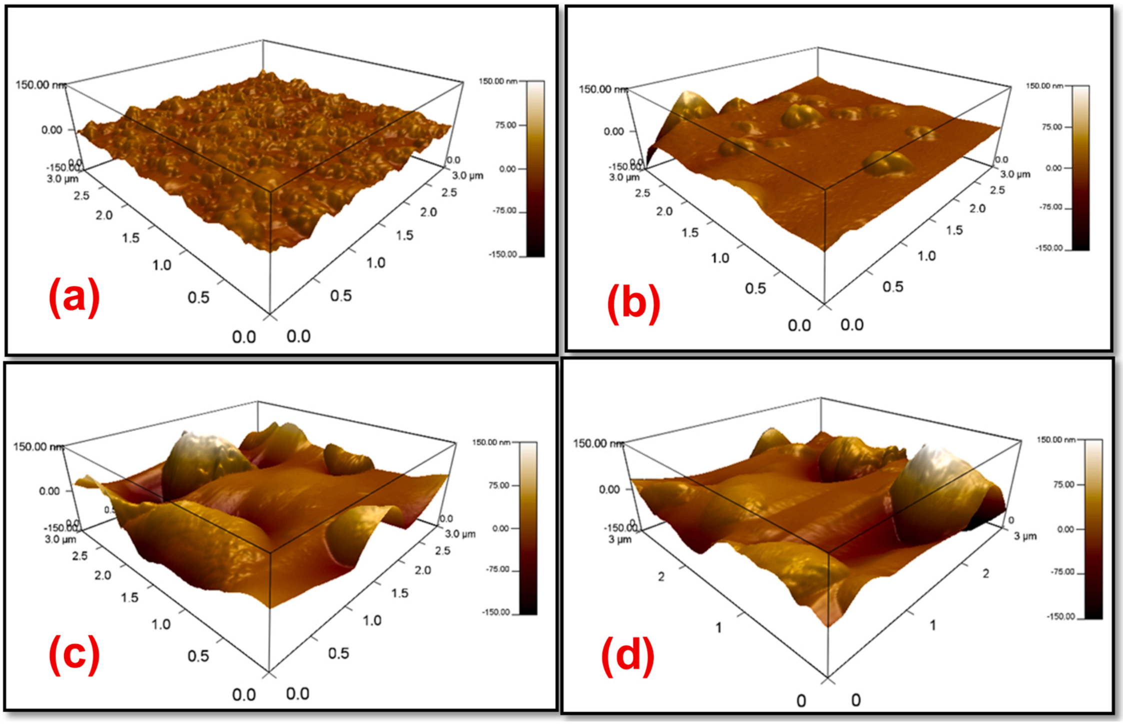
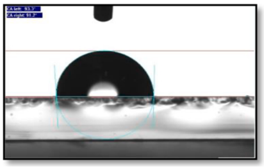
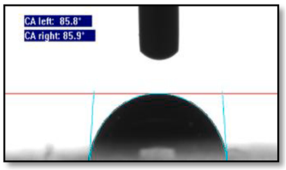
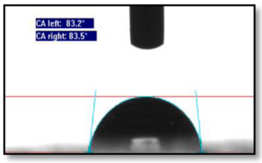
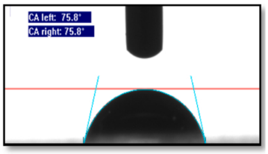
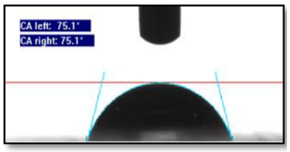
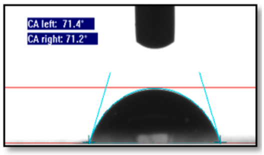


Fig. 4. Shows the AFM image of the PVDF- SPEEK blend films with SPEEK concentrations of (a) 5 wt%, (b) 7.5 wt%, (c) 10 wt%, and (d) 15 wt%.

different concentrations of SPEEK, while the PVDF concentration is kept constant at 2.5 wt% within the blend based on our previous optimization [23]. Fig. 3a and b show the FESEM analysis of PVDF-SPEEK blend films with SPEEK concentrations of 5 wt% and 7.5 wt%, respectively. The FESEM study reveals that PVDF-SPEEK (5 wt% and 7.5 wt%) blend films have uniform distributions of SPEEK with defect-free film surfaces. Fig. 3c and d show the SEM graphs of PVDF-SPEEK blend films with SPEEK concentrations of 10 wt% and 15 wt%, respectively. The FESEM study shows that as the concentration of SPEEK increases within the blend film, spherical structures appear on the surface of the film. This is due to some clusters of the sulfonic group (SO_3H) are present in the hydrophobic part or vice versa. As described by Dönmez et al. [24] at a higher concentration of SPEEK within the PVDF-SPEEK blend, the aggregation of spherical structure forms. They further studied the spherical surface by EDX analysis, and results show that these spherical structures have a higher concentration of sulfur.

AFM analysis conducted to examine the surface roughness further and topography of PVDF-SPEEK blend with different concentrations of SPEEK (5, 7.5, 10, and 15 wt%). Fig. 4a represents the AFM image of the PVDF-SPEEK blend (2.5 wt%-5 wt%). It is observed that the surface of the blend film is uniform and homogenous. The root means square (rms) roughness value of PVDF-SPEEK (2.5 wt%- 5 wt%) found to be 9.54 nm. As the concentration of SPEEK increases to 7.5 wt% (4b), 10 wt% (4c), and 15 wt% (4d), the rms roughness value of the sensing film increases to 14.974 nm, 35.267 nm, and 39.74 nm respectively. At higher concentrations of SPEEK, agglomerated spherical particles formed on the surface of blend film, as shown by FESEM analysis. These spherical particles increase the surface roughness of the PVDF-SPEEK films at the higher concentration of SPEEK [25]. Due to poor dispersion of PVDF and SPEEK blends, at higher concentration of SPEEK the surface of the blend membrane become non-homogenous and irregular. Therefore, based on FESEM and AFM analysis PVDF-SPEEK (2.5 wt%- 5 wt%) blend films are selected for further investigations. The nanoindentation characterization were also performed to study the mechanical properties the

Table 1
Contact angle measurements of PVDF film, and PVDF-SPEEK blend films with different SPEEK concentrations.

Sample Type	PVDF Film	PVDF- SPEEK (2.5 wt%- 1 wt%) composite film	PVDF-SPEEK (2.5 wt% - 3 wt%)
Contact angle image			
Contact angle	92.25°	85.85°	83.35°
Sample Type	PVDF- SPEEK (2.5 wt%- 5 wt%) composite film	PVDF- SPEEK (2.5 wt%- 7.5 wt%) composite film	PVDF-SPEEK (2.5 wt% - 10 wt%)
Contact angle image			
Contact angle	75.8°	75.1°	71.3°

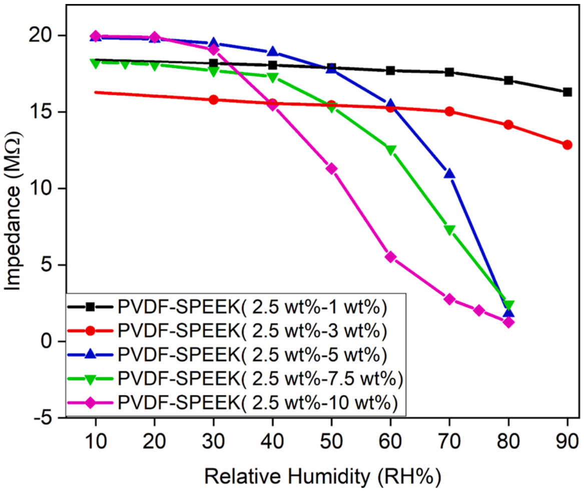


Fig. 5. Effect of relative humidity on the impedance of PVDF-SPEEK blend film sensors with constant PVDF concentration (2.5 wt%) and SPEEK concentrations varied (1, 3, 5, 7.5, and 10 wt%).

PVDF-SPEEK blend films as shown in Table S1 (supplementary data file).

3.3. Thermal stability analysis

The thermal stability of the PVDF-SPEEK composite blend studied by thermal gravimetric analyses (TGA). Fig. S1 shows the thermal behavior of PVDF-SPEEK blend films with different concentrations of SPEEK (1 wt %, 5 wt%, 7.5 wt%, and 10 wt%). The thermal degradation of PVDF-SPEEK blend composites exhibited three weight degradation steps in all the PVDF-SPEEK blend film concentrations (1, 5, 7.5, and 10 wt%). The initial weight loss of the PVDF-SPEEK blend is mainly due to the loss of adsorbed water vapors [26]. The second degradation step appears in the temperature range of 250–450 °C. This degradation step seems to be due to the diminishing of sulfonic acid groups within the SPEEK [24]. The third degradation step occurs beyond 500 °C. This degradation takes place due to the decomposition of the C—H and C—F bonds in the PVDF-SPEEK blend composite [27]. Fig. S1 also shows that the thermal degradation of PVDF-SPEEK blend composites (1, 5, and 7.5 wt%) occurs mostly at temperatures above 150 °C. It is also observed that as the concentration of SPEEK increases up to 10 wt%; more degradation occurs below 150 °C; hence more weight loss occurs.

3.4. Contact angle measurement

The hydrophilicity of the film indicates that the sensing film adsorbs water drops on the surface of the polymeric film. The contact angle of water drops on the surface of the sensing film measured by the sessile drop method. Table 1 shows the contact angle measurements of the PVDF, PVDF-SPEEK blend films with varying SPEEK concentrations. The contact angle of pure PVDF is 92.25° shows, obviously its hydrophobic nature. As the SPEEK blended with PVDF, the hydrophilicity of the PVDF-SPEEK blend film increases. The contact angle of PVDF-SPEEK (2.5 wt%, 1 wt%) blend film decrease to 85°. As the concentration of SPEEK increases further to 5 wt%, its contact angle decreases to 75.8°. The contact angle further decreased to 71.3° at to 10 wt% SPEEK concentration. This decrease in the contact angle of the PVDF-SPEEK blend film is mainly associated with the increase in the sulfonic group in the PVDF-SPEEK blend. The sulfonic group is hydrophilic; hence the addition of SPEEK increases the water adsorption affinity on the surface of the PVDF-SPEEK blended film, which is in agreement with the TGA results.

3.5. Impedance response

The electrical response of the PVDF-SPEEK blend film based resistive humidity sensors investigated. Fig. 5 shows the impedance response of PVDF-SPEEK blend humidity sensors with different concentrations of SPEEK. The impedance of the PVDF-SPEEK blend decreases with an increase in relative humidity level from 10 %RH to 90 %RH. This decrease in impedance associated with an increase in conductivity of the composite films as water vapor adsorbed on the surface of the PVDF-SPEEK blend. As the concentration of SPEEK increases from 1 wt% to 10 wt%, the sensitivity of the resistive humidity sensors increases as well. The PVDF-SPEEK blend based impedance humidity sensors with higher SPEEK concentrations (5 wt%, 7.5 wt%, and 10 wt%) is more sensitive to lower humidity levels as compared to those with lower concentrations of SPEEK (1 wt% and 3 wt%). The increase in the concentration of SPEEK within the blend membrane increases the concentration of the hydrophilic sulfonation group (SO_3), which enhances the absorption of water vapor on the surface of the sensing film, hence the sensitivity of the humidity sensor increases. This rise in the absorption of water molecules on the surface of the blend film at a higher concentration of SPEEK (7.5 wt% and 10 wt%), also increases the hysteresis loss of the PVDF-SPEEK impedance sensor as shown in the supplementary Fig. S2.

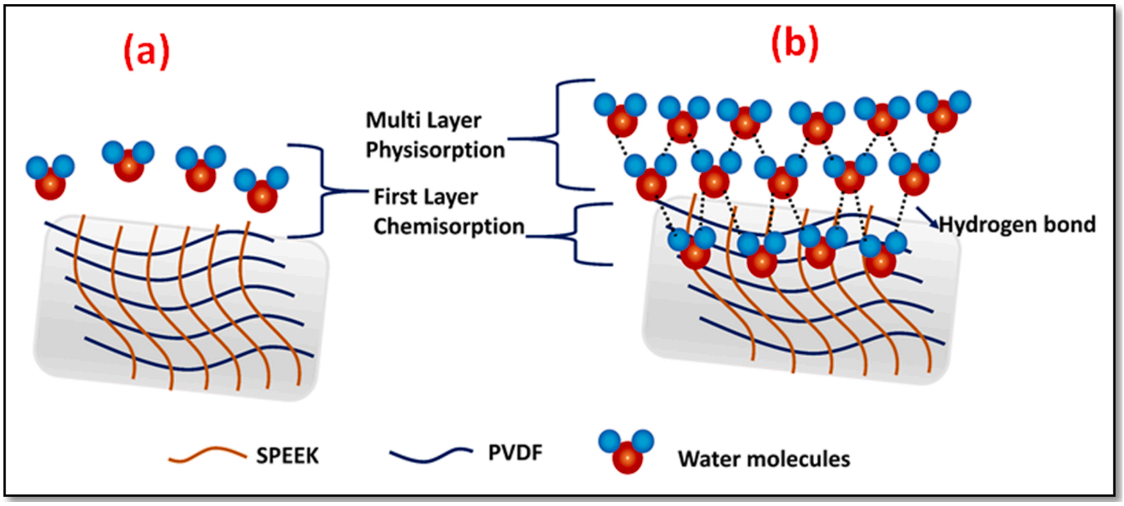


Fig. 6. Schematic of the mechanism for sensing (adsorbing) water molecules on the PVDF/SPEEK surface at (a) low RH (b) high RH.

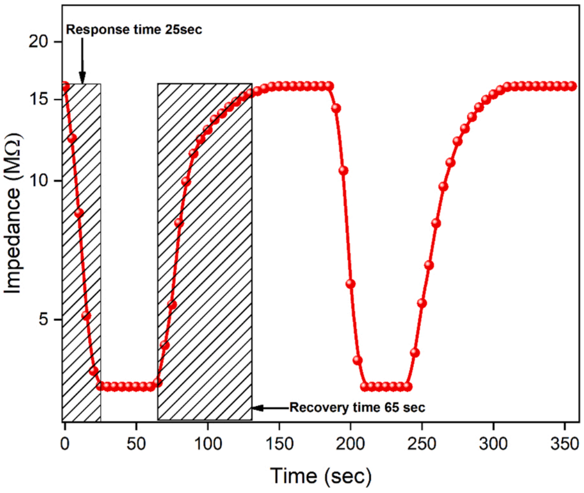


Fig. 7. Response and recovery cycles (40- 90 %RH) of PVDF-SPEEK blend (5 wt %) based resistive humidity sensor. The thickness of the optimized PVDF-SPEEK (5 wt%) blend films were measure using a profilometer and its average value was found to be 216 ± 20 nm.

Table 2
Response and recovery time of PVDF-SPEEK blend resistive humidity sensors.

Material	Fabrication Method	Response time (Sec)	Recovery time (Sec)
SPEEK [17]	Spin coating	100	105
Sulfonated polystyrene polymer [16]	Dip coating	30	300
Sulfonated polymer aromatic electrolytes (PAEK-SO3Na-x) [31]	Dip coating	90	100
PVDF-SPEEK (5 wt%) (Present work)	Spin coating	25	65

3.6. Humidity sensing mechanism

The sensing mechanism can be explained based on the interaction of PVDF-SPEEK with water molecules. The mechanism of humidity sensing on PVDF-SPEEK blend polymer composites shown in Fig. 6. At low humidity level (Fig. 6a), a small number of water molecules get adsorbed on the surface to create a first chemisorbed layer. As the relative humidity level increases (Fig. 6b), multilayer water adsorption developed, and it shows a liquid-phase-like behavior. A strong electrostatic field formed between the first chemisorbed layer and the incoming water molecules due to the accumulation of the high amount of water molecules. The corresponding physisorbed layers are stacked up and produce hydronium ions [28]. These H_3O^+ molecules between adjacent other water molecules, causing a further decrease in its resistance and increase in sensing response [29,30].

The response and recovery times of resistive humidity sensors are also essential parameters in determining the performance of the sensors. The response time of the humidity sensor defined as the time taken by the sensor to attain 90 %RH (in the current study: 40–90 %RH). The recovery time defined as the time that a sensor requires to reach the initial RH level (in this case, 40 %RH) from 90 %RH. Fig. 7 shows the response and recovery curve of the PVDF-SPEEK (5 wt%) based resistive sensor, the curve shows a repeatable and stable response. The response and recovery times of the PVDF-SPEEK (5 wt%) blend resistive sensors computed to be 25 s and 65 s, respectively. Table 2 summarizes the response and recovery times of different conductive polymer-based resistive humidity sensors. Compared with other reported polymeric humidity sensors, the PVDF-SPEEK (2.5 wt% - 5 wt%) based resistive humidity sensor shows faster response and recovery time. The optimized concentration of SPEEK (5 wt%) and PVDF (2.5 wt%) within the blend improved the resistive humidity sensor sensitivity at a lower humidity level and reduced the response and recovery time of the resistive humidity sensor.

4. Conclusion

The spin coating technique fabricated PVDF-SPEEK blend based resistive humidity sensors. The morphology of the PVDF-SPEEK blended film investigated by FESEM and AFM analyses. The results showed that at higher concentrations of SPEEK (10 wt% and 15 wt%), the distribution of SPEEK is not homogenous due to a higher amount of SO_3H group present within the PVDF-SPEEK blend. Also, when the concentration of SPEEK within the blend film increased the hydrophilicity of the sensing film also increased, which improved the sensitivity of sensors at lower humidity levels. The PVDF-SPEEK (5 wt%) blend resistive sensors showed higher sensitivity; also, the response and recovery times of the PVDF-SPEEK (5 wt%) blend resistive humidity sensor estimated to be 25 s and 65 s, respectively. These results indicate that the blending of SPEEK within the PVDF significantly improves the performance of the humidity sensors, but an optimum SPEEK concentration of 5 wt% recommended.

Declaration of Competing Interest

The authors report no declarations of interest.

Acknowledgments

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mtcomm.2020.101601.

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