



## Polyvinylidene fluoride shape memory polymer for dielectric device applications

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Shape memory polymers (SMPs) are emerging smart materials that can change their shape with the help of an external stimulus. A wide variety of stimuli can be used, including heat, light, pH, electric and magnetic field, from temporary to permanent shape, which affect the shape memory behavior of SMPs. Thermally induced shape memory behavior has been investigated in many studies. Polyvinylidene fluoride (PVDF) based polymers are an important class of electroactive smart materials that exhibit pyroelectric, ferroelectric and piezoelectric properties [1-3]. The shape memory properties of PVDF were investigated. Firstly, shape memory film was prepared by solvent casting method. The recovery and fixity behaviors of the PVDF polymer were investigated for various recovery times.

**Keywords:** PVDF, Shape Memory, Dielectri, Optic

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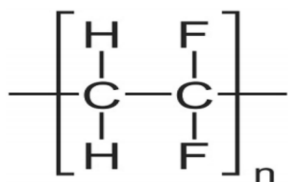
### 1. Introduction

Shape memory polymers (SMPs) are important smart materials with the ability to change their shape in a controlled manner. Shape memory polymers are used in many applications such as artificial muscles, 3D printers, soft robotics, biomedical applications, drug delivery applications, stents. SMPs with different characteristics are required to fulfill the demands of various applications. Polymers with SMP properties were introduced in the 1980s, and interest in these "smart" polymers continues to grow to this day. SMPs have many advantages due to their controllable shape recovery, elastic deformation, transition temperature, easy processing, low density, low cost, and being biocompatible and biodegradable [1-5].

Shape memory polymers (SMPs) are elastic structures equipped with sensitive switches that respond to appropriate stimuli. Shape memory effect (SME) can be induced by infrared light heating, electric resistance heating, light, magnetic field heating, water, solution and heat. PVDF is a popular option as SMPs due to its versatility and ease of preparation. At the same time, SMP materials have disadvantages such as low stiffness, low strength, and

inherent insulation properties that limit their development and applications. To overcome these disadvantages, much work has been done to improve the mechanical properties of SMP polymers. Shape memory effect is observed in polymers such as poly(vinylidene fluoride) (PVDF) with thermal excitation by heating above the transition temperature of polymers such as glass transition temperature or melting temperature [5-9]. The reason for using PVDF in this study is that PVDF and its copolymers are an important class of electroactive smart materials that exhibit pyroelectric, ferroelectric and piezoelectric properties. These electroactive polymers convert electrical energy into mechanical energy or vice versa. They are of interest in a wide range of applications, such as artificial mussels, tissue scaffolds and wearable sensors. PVDF is thermoplastic material. PVDF is also known as fluoropolymer and poly (1,1-difluoroethylene), denoted by (CH<sub>2</sub>-CF<sub>2</sub>) as a repeating unit in the molecular structure. It is one of the hardest, most widely used high purity synthetic materials in the world. Compared to other fluoropolymers such as polytetrafluoroethylene (Teflon), PVDF has a low density (1.78 g/cm<sup>3</sup>). It is widely accepted

and preferred for applications due to its mechanical and thermal strength, magneto-electric properties as well as its ability to be used in solid and liquid coating forms [9-11].



**Figure 1.** Structural formula of PVDF

Polyvinylidene fluoride, first produced in 1969, is also known as polyvinylidene difluoride, PVF<sub>2</sub> and its popular trade name Kynar®

It is widely used in the chemical, semiconductor, medical and defense industries, as well as in lithium-ion batteries. It is also increasingly used in aerospace applications. Having a high decomposition temperature, indefinitely stable compared to other materials, and being inert to everything carries an excellent cost/performance ratio. It can also be used in repeated contact with food products, as it is non-toxic. PVDF has a remarkable property for electricity generation. It can be used in traffic sensors and pressure sensors in various applications due to its properties such as sound, force, pressure, heat or acceleration. It also responds very well to heat and airflow. thus also used in nasal thermal airflow monitoring [8-12].

## 2. Material and Methods

Approximately 1.3 g of (PVDF) Polyvinylidene fluoride powder, taken in 4:1 ratio, was mixed in the mixture of chloroform: DMF solution on a magnetic stirrer at 80 degrees until it became a clear solution, then poured into a petri cape and dried at low temperature for 2 days. Polymer films with a thickness of about 0.15mm were produced. The real dielectric constant ( $\epsilon_r$ ) was calculated with the help of the thickness of the polymer film. The obtained polymer film was cut appropriately and shape memory test, FTIR, UV and dielectric analyzes were performed.

### 2.1. Shape Memory Test and Characterization

For the shape memory test, which consists of 3 steps such as folding, application and looking at the shape memory feature, first of all, PVDF polymer film was cut into a rectangular shape. The PVDF polymer film is shaped when heated slightly above the glass transition temperature (T<sub>g</sub>). Once shaped, it is left in the refrigerator for a while to retain its shape, then heated to see if it remembers its original shape, the flat rectangular shape. For the shape memory test, after PVDF was heated at the glass transition temperature (130°), it was placed in a mold as in the figure below, and it was allowed to take its deformed shape. After keeping it in the refrigerator for about 15 minutes to take its shape with the mold, it was taken out of the mold and placed on the hold plate to remember its old shape, and a memory test was

performed at a temperature slightly above the T<sub>g</sub> glass transition temperature.



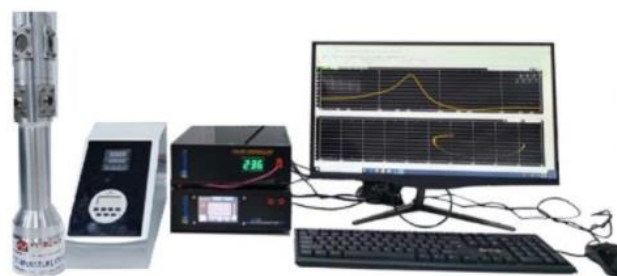
**Figure 2.** Structural formula of PVDF

$$R_r = \frac{\theta_{\text{constant}} - \theta_{\text{end}}}{\theta_{\text{constant}}} \times 100 \quad (1)$$

$$R_f = \frac{\theta_{\text{constant}}}{\theta_{\text{max}}} \times 100 \quad (2)$$

By calculating the time-varying angle values, shape stability (R<sub>f</sub>) and shape recovery (R<sub>r</sub>) rates were calculated with the help of the above equations.

The dielectric properties of the PVDF shape memory polymers film were characterized by the fytronix dielectric analyzer system. Real dielectric constant, virtual dielectric constant, cole cole curve, conductivity and recycling rate graphs of PVDF were drawn by using the obtained data.



**Figure 3.** Fytronix dielectric constant analyzer system.

## 4. Results and discussion

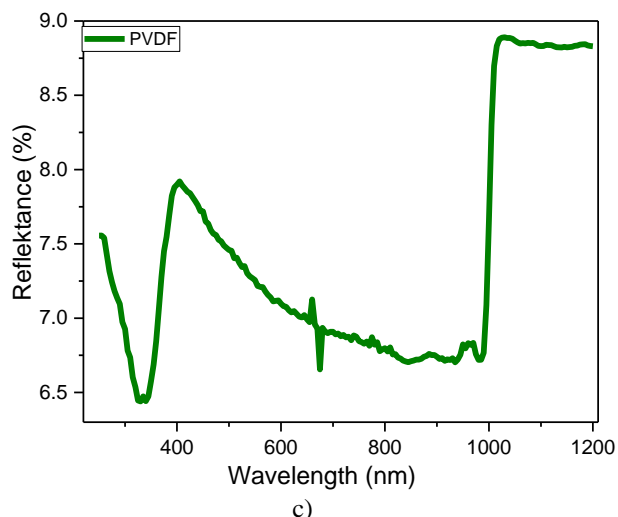
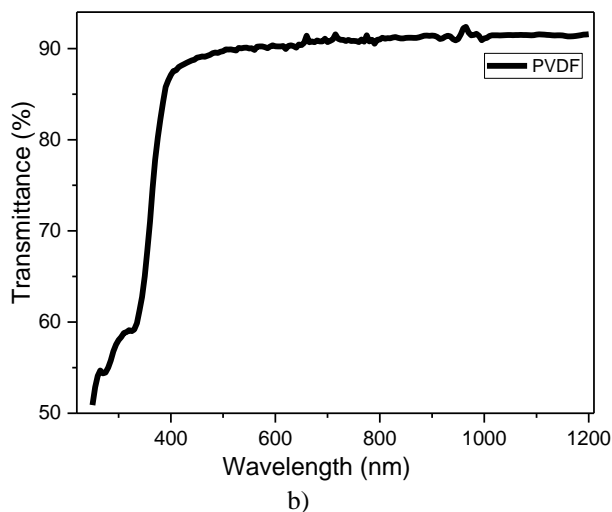
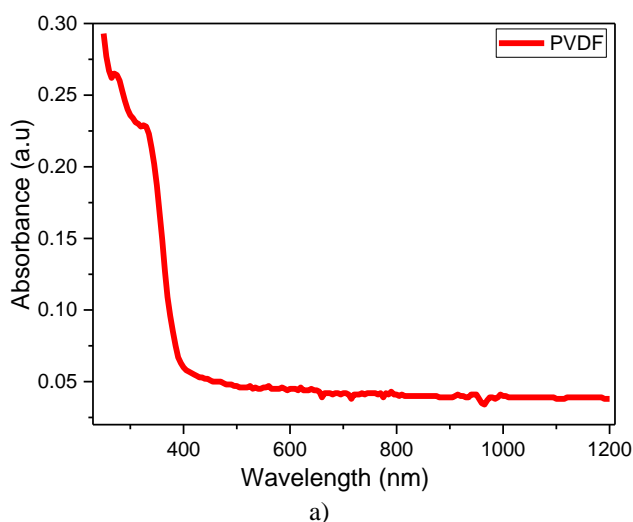
The absorbance curve of PVDF is given in Fig.4a and the absorbance peak is observed about 323 nm. The transmittance curve of PVDF is shown in Fig. The transmittance edge is approximately 374.5 nm and the transmittance value is approximately 88.5%, indicating that the transparency of PVDF is well. The reflectance curve of PVDF is shown in Fig.4c. The reflectance plots showed that the reflectance value of PVDF was consistent with the literature.

The FTIR (Fourier Transformation Infrared Spectrum) plot of PVDF shape memory polymer film is shown in Fig.5. As seen in Fig.5, the characteristic peak values of PVDF indicate the presence of 3022 cm<sup>-1</sup> CF<sub>3</sub> vibrations, 1200 cm<sup>-1</sup> CF<sub>3</sub> group and 1000 cm<sup>-1</sup> CH<sub>2</sub> bond group. For the spectra of PVDF film before modification, the characteristic absorbance peaks at 3022, 2980, 1673, 1402, and 878 cm<sup>-1</sup> correspond to the

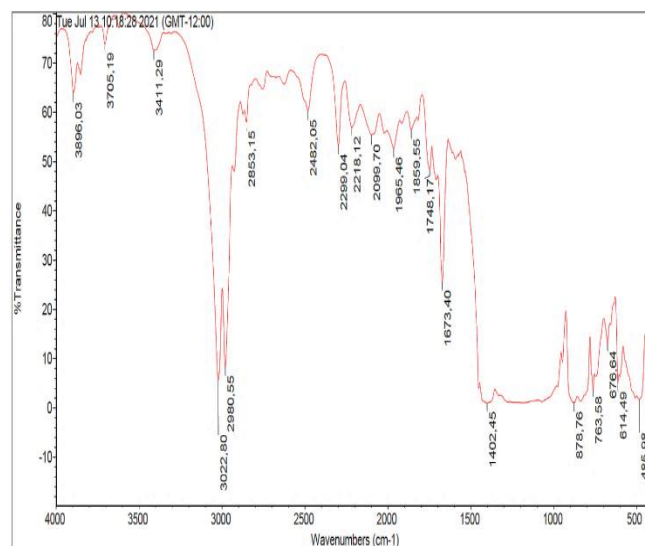
stretching vibration of CF<sub>2</sub>, symmetric stretching vibration of CH<sub>2</sub>, deformation vibration of CF<sub>2</sub>, stretching vibration of CF<sub>2</sub> and the amorphous region of PVDF, respectively, indicating the film before modification still contain the characteristic functional groups of PVDF (Zhou et al., 2019) [12-13].

On the other hand, it is well known that materials with high dielectric constant have high energy loss as well as high absorbency. As seen in Fig.6, the dielectric constant of the polymer is decreased as the frequency increases. This means that the dielectric behaviour exhibit a dissipative behaviour. The change in the dielectric constant of PVDF is due to electrical polarization [6,10].

The alternating current conductivity,  $\sigma_{ac}$  of the PVDF is measured from 1kHz to 5 MHz and it  $\sigma_{ac}$  changes depending on the frequency. Since the conductivity increases linearly as the frequency value increases, there is no dc conductivity, that is, it does not have dc electrical conductivity. The linear change in the alternatig electric conductivity suggests that the polymer is an insulating material.



**Figure 4.** UV spectroscopy analysis for PVDF a) Absorbance b) Transmittance c) Reflectance



**Figure 5.** FTIR pattern of the PVDF.

The dielectric behaviour of the polymers are important for dielectric device applications. Also, the dielectric properties of the PVDF based polymers are changed with shape memory behaviour of the polymers. The complex dielectric function is defined by the following relation

$$\epsilon^* = \epsilon_r + \epsilon_i$$

Where  $\epsilon_r$  is the real part of the dielectric constant and whereas  $\epsilon_i$  is the imaginary part which are defined by the following relations

$$\epsilon' = \frac{C \times l}{\epsilon_0 \times A}$$

1

$$\epsilon'' = \tan \delta \times \epsilon'$$

2

The alternating current conductivity of the polymer can be determined using impedance value of the polymer and it is given by the following relation

$$\sigma_{ac} = \frac{l}{Z \times A} \tag{3}$$

The real and imaginary parts of the PVDF polymer are shown in Fig. 6 and 7. The real part of the polymer exhibited a dispersive behaviour. This means that the dielectric constant is decreased with the increasing frequency. The dielectric constant of PVDF was found to be 4.5. The decrease in the dielectric constant of the PVDF polymer is due to the change in numbers of dielectric dipoles. The change in numbers of the dielectric dipoles creates a dielectric polarization. The dielectric polarization causes a change in the dielectric constant of the PVDF polymer. The numbers of the dielectric dipoles are decreased with the increasing frequency of applied electric field.

The imaginary part of the dielectric constant is increasing frequency and shows a dielectric peak. This peak is related to the dielectric relaxation mechanism.

The dielectric relaxation mechanism of the PVDF polymer can be analyzed by the following relation;

$$\epsilon^* - \epsilon_{\infty} = \frac{\epsilon_0 - \epsilon_{\infty}}{1 + (i\omega\tau_0)^{1-\alpha}} \tag{4}$$

where  $\epsilon^*$  is the complex dielectric constant,  $\epsilon_0$  and  $\epsilon_{\infty}$  are the “static” and “infinite frequency dielectric constants,  $\tau_0$  is the relaxation time and  $\alpha$  is an exponent ( $0 < \alpha < 1$ ).

In order to analyze the dielectric mechanism of the PVDF polymer, we plotted Cole–Cole plot, as shown in Fig. 8. The behaviour of the Cole–Cole plot determines the type of dielectric relaxation mechanism. As shown in Fig.8, the Cole–Cole plot suggests that the dielectric mechanism of PVDF polymer is a non-Debye type dielectric relaxation mechanism.

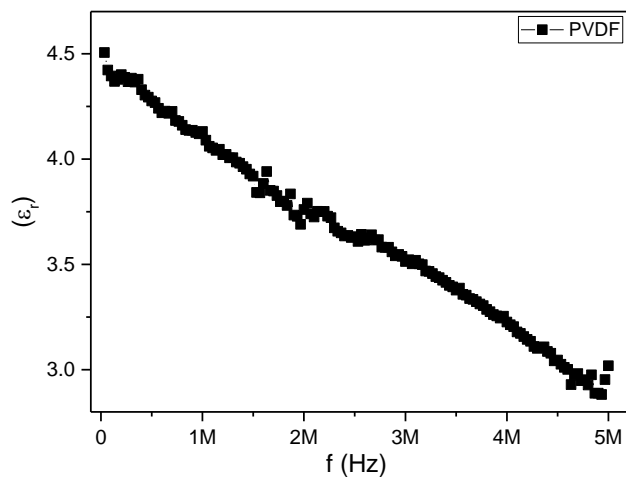


Figure 6. Relative permittivity vs. frequency plot of PVDF

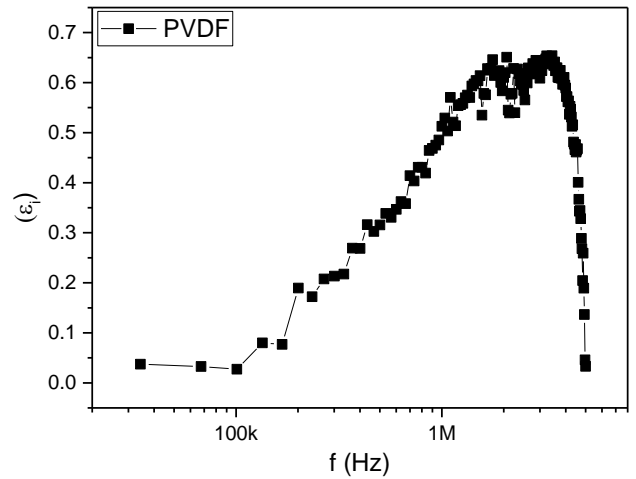


Figure 7. Dielectric loss vs. frequency plot of PLA

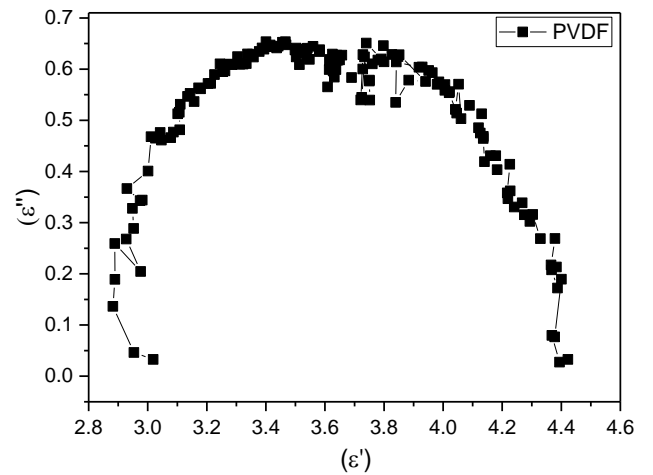


Figure 8. Cole–Cole plot of the PVDF

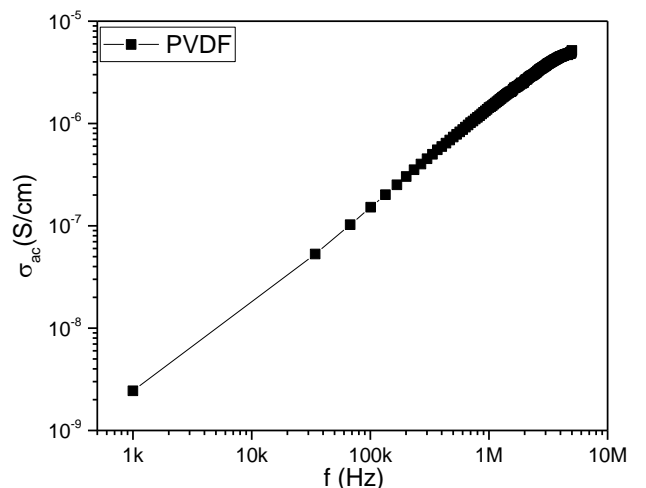


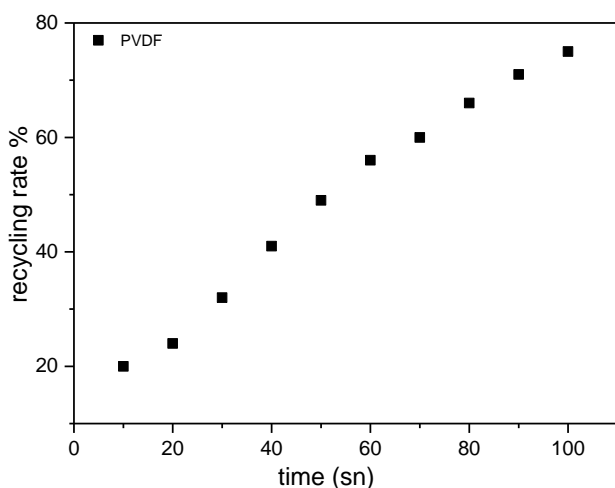
Figure 9. Plots of the alternating current conductivity vs. frequency.

In order to determine electrical conductivity type of PVDF polymer, the alternating current conductivity,  $\sigma_{ac}$ , is measured as a function of frequency. The alternating current conductivity plot of the PVDF polymer is shown in Fig.9. As

seen in Fig.9, the conductivity is linearly increases with frequency, suggesting that PVDF exhibited an insulating behaviour. Also, Fig.9 suggests that the polymer does not include a dc (direct) component. It is an insulating material. The determination of the conductivity mechanism of the PVDF was applied using the well known Jonscher relation;

$$\sigma_{ac} = \sigma_{dc} + B\omega^s \quad 5$$

where  $\sigma_{dc}$  is the direct current conductivity, B is a constant,  $\omega$  is the angular frequency and s is an exponent. The s values can be calculated from the slope of  $\log \sigma_{ac}$  vs.  $\log \omega$  plot.



**Figure 10.** Recycling rate vs. time plot of PVDF

When the PVDF film, which was modified in Figure 10, was placed on the hot plate set to the glass transition temperature, a graph was obtained against the amount of opening over time until it regained its former shape depending on time. (Fig. 10). In the graph obtained, the polymer film became stable after a while and a deformation close to its former shape was observed. The polymer showed the feature of remembering its old state at a rate of about 70%.

## 5. Conclusion

It was determined that the shape stability and shape recovery rate of the synthesized PVDF shape memory polymeric film was over 70%. Therefore, it can be said that this material is suitable for the production of shape memory materials and can be used in various medicine, industry and chemical fields. In addition, its dielectric properties show that PVDF can be polarized with the effect of external magnetic field, which shows that it can also be used in magno-electric applications.

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