



# INVESTIGATIONS OF OPTICAL, ELECTRICAL AND THERMAL PROPERTIES OF PIEZO PMMA/PVDF MEMBRANE AS ELECTRICAL AND ADVANCED ENERGY SAVING MATERIALS

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## ABSTRACT

Present work is aimed at developing electrical and energy storage component based on PMMA/PVDF blend. The film of PMMA/PVDF was prepared using solution casting method with a verity weight percentage of PVDF. Physical properties such as (absorption coefficient, extinction coefficient, refractive index and real and imaginary dielectric constants) have been studied. Some expository strategies, for example, FTIR spectroscopy, differential scanning calorimetry (DSC), were used to assess the compatibility of these two polymers. Results show that the (absorption coefficient, extinction coefficient, refractive index and real and imaginary dielectric constants are increased by increasing PVDF content. As well as the absorbance increased with increasing the amount of PVDF while transmittance decrease. Moreover, the electrical conductivity has been increased with increasing PVDF content.

**Keywords:** differential scanning calorimetry, PVDF membrane, expository strategies, optical, thermal, energy saving.

## 1. INTRODUCTION

A materials such as organic phase change materials (OPCMs), and advanced energy saving materials which have a high heat of melting is capable to storage or release a lot of "potential heat" when converted from physical condition into another condition, are probably the most encouraging thermal storage filters to control the use of volatile sources such as solar heat and geothermal energy, as well as attractive properties Such as safe to human, corrosion resistance, immediately accessible over a wide range of temperature, and possesses great thermal and chemical properties with super cooling or phase separation [1].

Composite materials have a huge range of use in the field of electronics, for example, solar cells, light-emitting diodes transmitted, transistors. PVDF is the most unsolicited semiconductor application from many other ferroelectric polymers because it has high stability for environmental conditions, high temperature resistance, and great processing capacity [2]. In addition, PVDF has been extensively tested for its electrophysiological and electrophoresis interaction in general and the effect of its polymorphic structures used as part of the electronic advance [3]. PVDF is generally used as part of transformers, Electro voltage sensors, and IR imaging. PVDF compared to other conventional materials recognized by ease of application at low temperature, flexibility, and good electrical properties [3].

PMMA has been widely used as part of optical material, lenses, and discs due to its hardness, transparency and yet hard molding [4]. Among many polymers, PVDF has good compatibility with PMMA with different concentration in the polymer mix [5]. This polymer mix combines the resistance to chemical film, durability, and PVDF electrolytic nature with good optical properties, low smoke damage, and high flexibility of the PMMA phase. These blends are attractive for commercial

suitability [6]. The aim of this study was to study and improve the ability to prepare a polymer mix to be used as an electrical conductor on surfaces and floors to show that electrolytic polymer materials can generate energy from inexhaustible sources, for example, rain drops and wind energy utilizing electro-cathode materials. [7]

## 2. MATERIALS AND EXPERIMENTAL METHODS

Polyvinylidene fluoride (PVDF) is a low-density, non-reactive, low-density polymer polymer (1.78 g / cm<sup>3</sup>) with a molecular size (16 microns) supplied from China Guangzhou Li Chang Fluoroplastics Co., Ltd, PMMA was purchased from the local market. Prepare samples were from PMMA and PVDF with different combinations (80/20, 60/40 and 50/50 w / w) by dissolving the polymer in DMF at 70 ° C on a magnetic stirrer after that cast on a petri-dish thereafter put in the air for Drying about 24 hours. It is then delivered in a discharged furnace at 90 ° C for about 72 hours for elimination of the solvent. Film thickness was in the 100-150 μm range.

## 3. CHARACTERIZATION

The optical properties of (PMMA/PVDF) blends are estimated by utilizing UV/1800/ Shimadzu spectrophotometer in range of wavelength (200-800) nm. The absorption coefficient ( $\alpha$ ) of (PMMA/PVDF) blend can determined by equation [1], [8]:

$$\alpha = 2.303A/t \quad (1)$$

Where

A: absorbance t: thickness of the specimen.

Regarding to amorphous materials the photon absorption is specified by the relation [6]:

$$\alpha h\nu = B(h\nu - E_g)^r \quad (2)$$



Where B is a constant,  $h\nu$  is the energy of the photon,  $E_g$  is the energy band gap,  $r = 2$  for allowed indirect transition and  $r = 3$  for the forbidden indirect transition.

The extinction coefficient ( $k$ ) is given by the following equation [9]:

$$K = \alpha\lambda/4\pi \quad (3)$$

The refractive index ( $n$ ) of blend is calculated by the following relation [10]:

$$n = (1+R/2)/(1-R/2) \quad (4)$$

Where ( $R$ ): the reflectance.

The dielectric constants (real ( $\epsilon_1$ ), and imaginary ( $\epsilon_2$ ) of (PMMA/PVDF) are calculated by following equations [10]:

$$\epsilon_1 = n_2 - k_2 \quad (5)$$

$$\epsilon_2 = 2nk \quad (6)$$

Optical conductivity ( $\sigma_{op}$ ) can be determines [10] as:

$$\sigma_{op} = \alpha nc/4\pi \quad (7)$$

Electrical conductivity can be calculated from the impedance as follow [11]:

$$\rho = R \frac{l}{A} \quad (8)$$

$$\sigma = \frac{1}{\rho} \quad (9)$$

Where  $R$  is the impedance,  $l$  is the length of the specimen,  $A$  cross section area  $\text{mm}^2$ .

For better understanding and confirmation to the functional groups existence in the PVDF and PMMA, the structural and chemical bond in the chains of the polymers can be studied through the characterization of the vibration modes by infrared spectroscopy An FT-IR analyzer (Nicolet iS10, USA) has been utilized. Samples were examined in the range from (500-4000) of wavelength.

The DSC analysis of PMMA/PVDF blends has been performed using a PerkinElmer (Norwalk, CT) DSC-7 differential scanning calorimeter operating on a UNIX platform with a heating rate of  $10^\circ\text{C}/\text{min}$  in the temperature range of  $50\text{--}250^\circ\text{C}$ .

## 4. RESULTS AND DISCUSSIONS

### 4.1 UV-visible

Figure-1 demonstrates the absorptivity spectra for (PMMA/PVDF) polymer blends with a wavelength of the incident light for various weight percentage of PVDF. As it is clear from the figure, the prepared annealed membrane demonstrate an increment in the absorption for all the prepared specimens of polymer blends at UV zone, this is because of the excitation of giver level electrons to

the conduction band at given energy[10]. The investigated specimens demonstrate a strong absorption and move in the retention band edge towards a higher (optical) wavelength; hence, three maxima at (378,388,402) were seen [12].

Moreover, these shifts in the absorption band edge reveal the interaction between PMMA and PVDF in accordance with FTIR and DSC results [12]. The absorbance of the prepared samples (PMMA/PVDF) is increased with increasing the concentration of PVDF. This absorbance has led to increasing the numbers of gathered photons and subsequently, the number of produced holes in the buffer layer enhanced the photocurrent of the organic solar cells [13].

Obviously, a few blends display an all-around characterized window of wavelength 350-420 nm. A severe and exceptional height of this window is seen in the mix (50/50). The current window of conductivity can be utilized as an optical sensor or passageway channel for the wavelength 350-420nm in the UV and VIS districts.

Figure-2: reveals spectra of transmittance of (PMMA/PVDF) membrane with wavelength of the incident light. From the figure, spectra of transmittance of the prepared membrane reduced with increasing PVDF weight percentage.

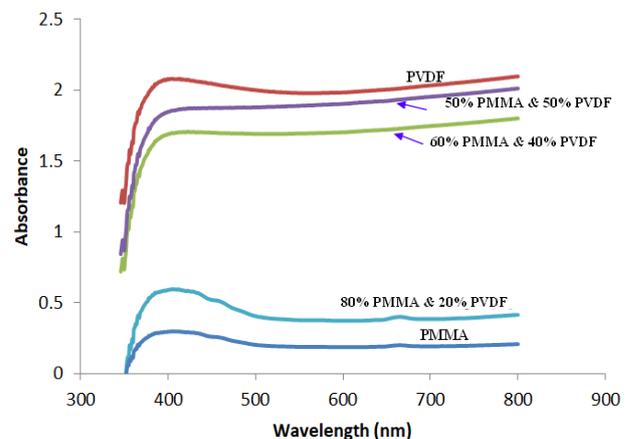


Figure-1. Variation of absorbance for (PMMA/PVDF) with a wavelength.

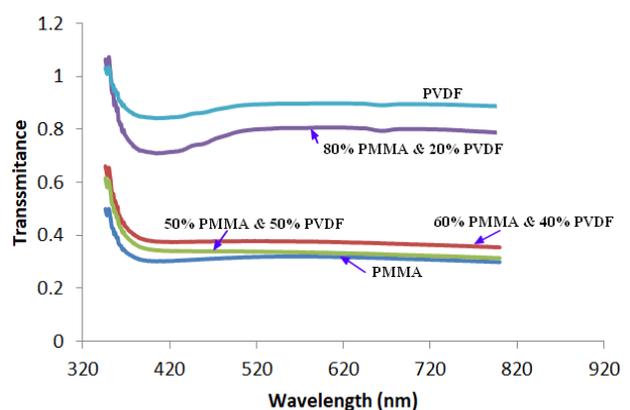
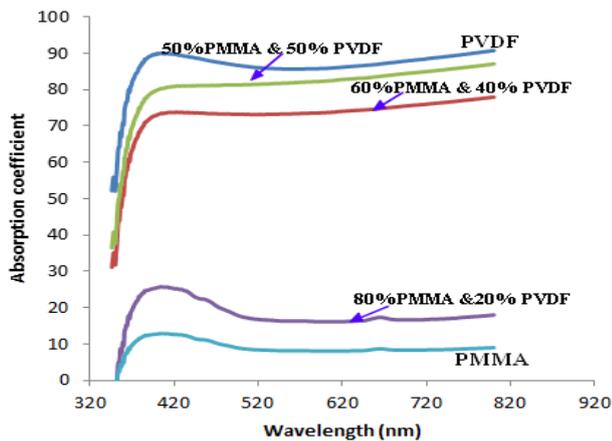


Figure-2. Variation of transmittance for (PMMA/PVDF) with a wavelength.

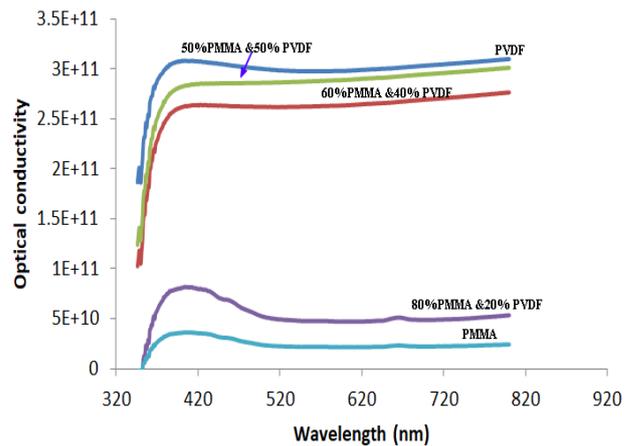


The factor of absorptivity help to understand the idea of the electron movement the magnitude of the absorption coefficient of (PMMA/PVDF) membrane less than  $a[10^4 \text{ cm}^{-1}]$ , so the electron suffering an indirect transmittance as shown in Figure-3. electronic transition (K band) of carbonyl groups  $\pi - \pi^*$  lead the absorption coefficient of (PMMA/PVDF) membrane to show a shoulder-like band at 402,406 and 408nm, separately and raised with increasing the concentrations of PVDF, this might be because of increasing the number of charge bearers, subsequently, increment the absorbance of (PMMA/PVDF) and absorption coefficient [14].



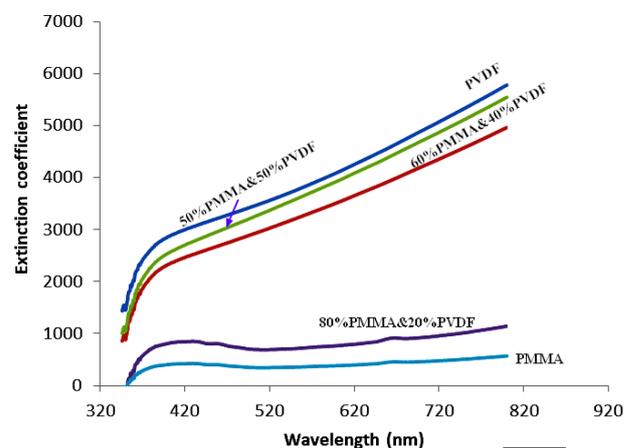
**Figure-3.** Variation of absorption coefficient ( $\alpha$ ) for (PMMA/PVDF) with wavelength.

Figure-4 represents the optical conductivity of (PMMA/PVDF) membrane with wavelength for different concentrations of PVDF. From figure it is clear that increasing PVDF concentration leads to enhancement of the optical conductivity which may be due to the creation of restricted levels in the energy gap; the increase of piezoelectric PVDF concentrations has led to improvement of the density of localized states in the band structure, so this will enhance the absorption coefficient consequently increasing the optical conductivity of (PMMA/PVDF)" [15]. The high optical conductivity of the prepared samples of polymer blend at a low wavelength of photon and then the reduction with increasing wavelength is due to the reason that optical conductivity relies substantially on incident radiation through samples of (PMMA/PVDF) which increases the charge transfer excitations. From Figure-4 the spectra demonstrated that the prepared samples could be transmittance near infrared region and within the visible region [16].



**Figure-4.** Represent the change in optical conductivity (PMMA/PVDF) with wavelength.

Figure-5 represents the change in extinction coefficient for (PMMA/PVDF) with wavelength. It is obvious from figure5 that the extinction coefficient increments with increment in PVDF weight percentage, which results in improvement of absorption, the cause of homogenous (PMMA/PVDF) polymer blend according to FTIR and DSC results. The high values at UV region of extinction coefficient as represented in the figure is due to high absorptivity of the prepared samples. Moreover, the increments in extinction coefficient with wavelength at visible and close IR locales cause of the increase in absorption coefficient at visible and close infrared area, therefore, the extinction coefficient value increased with increasing wavelength in accordance with Equation. (3) [17].



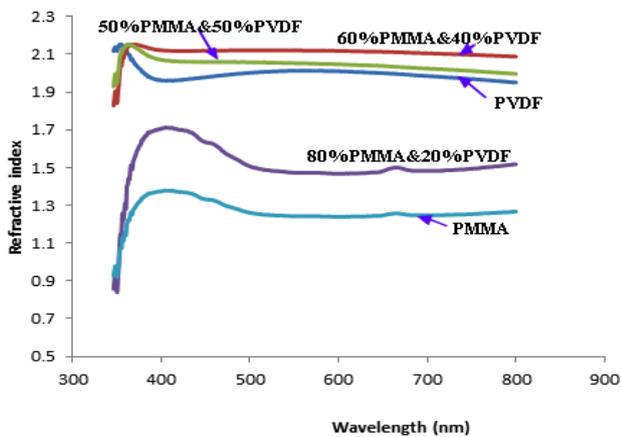
**Figure-5.** Change in extinction coefficient for (PMMA/PVDF) with wavelength.

Figure-6 demonstrates the spectra of refractive index in the range 350- 800 nm atmosphere temperature for all prepared film. It is obvious from the figure it included a intense band at 350nm alongside the shoulder - like the band a round 375-400 nm. In this way, the mixing of PVDF with PMMA can make the refractive index become higher with diminishing wavelength and the change was clear at shorter wavelengths demonstrating the



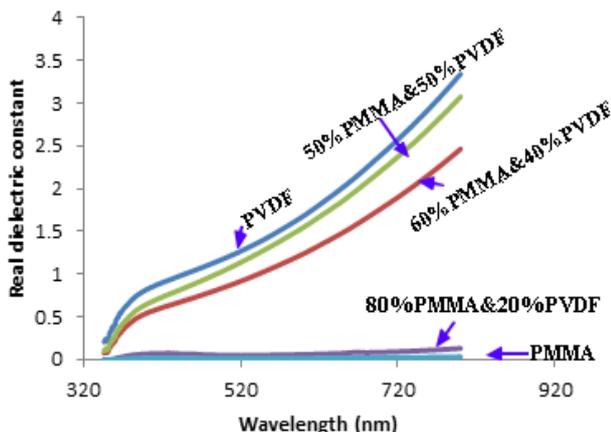
regular state of a scattering curve. It should be fixed that the estimations of the refractive index of blend repose in the middle of the estimations of homopolymers. Additionally, the refractive index of the prepared specimen improved when PVDF concentration increased.

The reliance refractive index on composition caused by the interaction phenomena because of the molecular orientation, processing conditions and domain structure [14]. The extremely significant magnitudes of the refractive index might be due to an increment in the valence intensity of charge transporters.



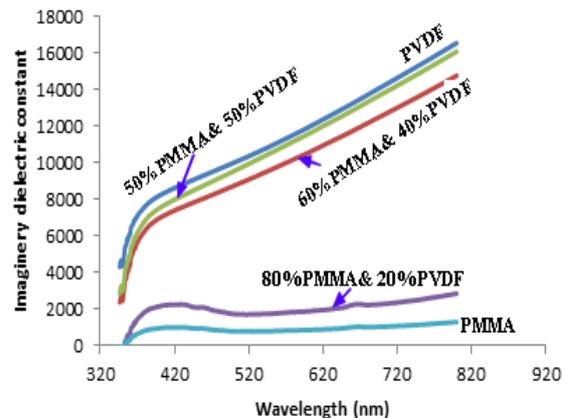
**Figure-6.** Variation of refractive index of (PMMA/PVDF) with wavelength.

Figure-7 and Figure-8 demonstrate the conduct of real and imaginary parts of the dielectric constant of (PMMA/PVDF) membrane as a function of wavelength for different PVDF concentrations respectively. From the figures, the clear trend of all the prepared membrane was that the ( $\epsilon_1$ ) and ( $\epsilon_2$ ) parts of dielectric constant for (PMMA/PVDF) membrane show a significant increase with the increment PVDF concentrations as compared to pristine PMMA. Moreover, the behavior of the real and imaginary part of dielectric constants also show an extreme increase with investigated wavelength.



**Figure-7.** Change of ( $\epsilon_1$ ) dielectric constant for (PMMA/PVDF) polymer blend with wavelength.

This behavior revealed by Figure-7 and Figure-8 could rely on the effect of PVDF concentration and polymorphous changes of PVDF from  $\alpha$  to  $\beta$  polymorph which could affect on electrical polarization that increases the charge polarization and hence increases both the ( $\epsilon_1$ ) and ( $\epsilon_2$ ) parts of the dielectric constant of (PMMA/PVDF) membrane [18].



**Figure-8.** Change of ( $\epsilon_2$ ) dielectric constant for (PMMA/PVDF) polymer blend with wavelength.

#### 4.2 FTIR spectroscopy analysis

The FTIR spectra figure 9 with regard to the PMMA cast in DMF, a strong peak has been noticed at  $750 \text{ cm}^{-1}$  show distinguishing vibration the  $\rho$  ( $\text{C-H}_2$ ); The C-O-C bond (ether ester) is appeared by the existence of peaks at  $1152$  and  $1257 \text{ cm}^{-1}$ . The peaks at  $1439$  and  $1457 \text{ cm}^{-1}$  refer to bonds of C-H and the one at  $1722 \text{ cm}^{-1}$  is a consequence of the essence of the carbonyl groups ( $\text{C=O}$ ). The vibration at  $2860$  and  $2932 \text{ cm}^{-1}$  separately reveals -CH extending peaks which is symmetric and asymmetric. From the spectra of casted PVDF shown in Figure-9, different absorption bands are assigned, and the asymmetric and symmetric stretching vibrations of the  $\text{CH}_2$  group are shown, respectively at  $3027 \text{ cm}^{-1}$  and  $2987 \text{ cm}^{-1}$ . Three intense peaks have been noticed in the range of  $1535$ ,  $925$  and  $678 \text{ cm}^{-1}$ .

The previous two peaks were allocated because of the C-F extending vibration and the last one peak was allocated because of the C-C bond of the PVDF. The DMF is additionally the wellspring of the event of the extending vibration of  $\text{C=O}$  amide  $1773 \text{ cm}^{-1}$  and for the PVDF and, distinctive absorption groups were allocated to various crystalline PVDF polymorphs, the peaks height at  $765 \text{ cm}^{-1}$  ( $\alpha$ -shape) and  $850 \text{ cm}^{-1}$  ( $\beta$ -frame) were observed.

This characterization of FTIR analysis for the casted PVDF in DMF is decent concurrence with the outcomes from past studies [19]. Figure-9 shows the IR spectrum of the second group of the polymer blend. FTIR results of PMMA/PVDF blend demonstrated the spectral overlay of the considerable number of syntheses where the relegation of any chemical interaction between the two polymers. These polymer blends have a very similar structure to the infrared spectrums of PMMA polymer, and it cannot observe any significant differences between these



IR spectrums, except the intensity for all characteristic peak of the polymer blend is lower than their counterparts

of base casted PMMA.

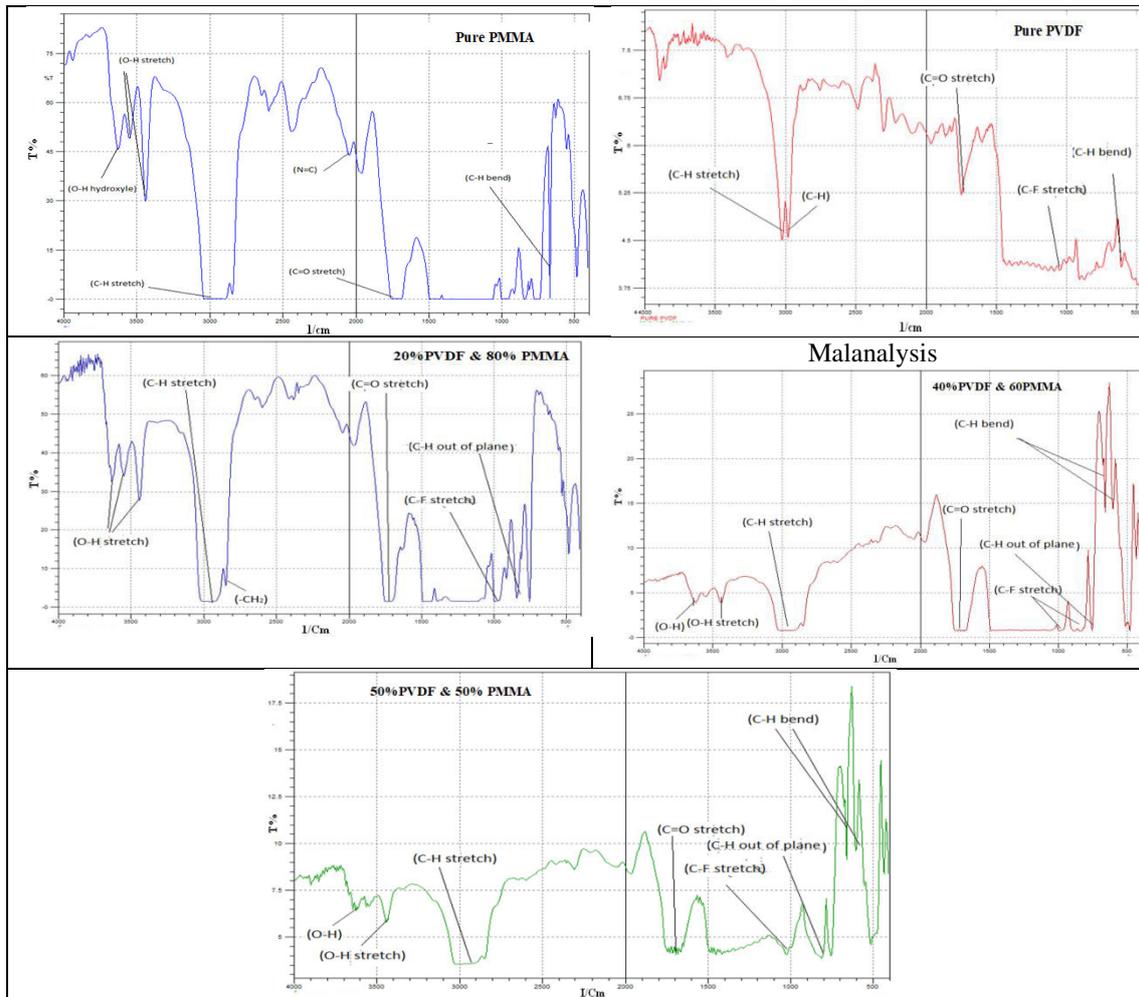


Figure-9. FTIR analysis of pure PMMA, pure PVDF and (PMMA/PVDF) polymer blends.

#### 4.3 DSC analysis

The DSC thermal analysis of all the prepared blends were examined utilizing DTA from 25 °C temperature to 250 °C. DTA thermograms have shown in Figure-10. The melting temperature ( $T_m$ ) is ascribed to a sharp endothermic peak. In DSC peak, the pure PVDF demonstrated the double melting peaks which have been revealed by DSC test on PVDF due to the variety of polymorphs distinctive to PVDF, which concurred with information from the literature [19,20] support this concept. In particular, the low-temperature melting peak which specified from thermograms closed to 130 °C, is a melting point of  $\alpha$ -polymorph crystals, while the  $\beta$ -polymorph crystals melt at the high-temperature peak, at about 175 °C [21].

Obviously, the dissolving temperature of PMMA/PVDF mixes increased somewhat with a small concentration of PVDF. For instance, the melting temperature of PMMA/PVDF (80/20) blends raised to 174.78 °C, is 8 °C higher, compare with neat PMMA. The region under the curve endothermic melting is regarding the level of crystallinity. It is clear that the level of crystallinity for the blends are decreased for low concentration of PVDF content and the melting temperature, in counterpart blends the melting temperature reduced and the crystallinity increased. Acceptable miscibility between PVDF and PMMA are related to the spectacular change in crystallinity and melting temperature. Therefore, it is clear that PMMA is mostly amorphous and is not related to the heat of melting.

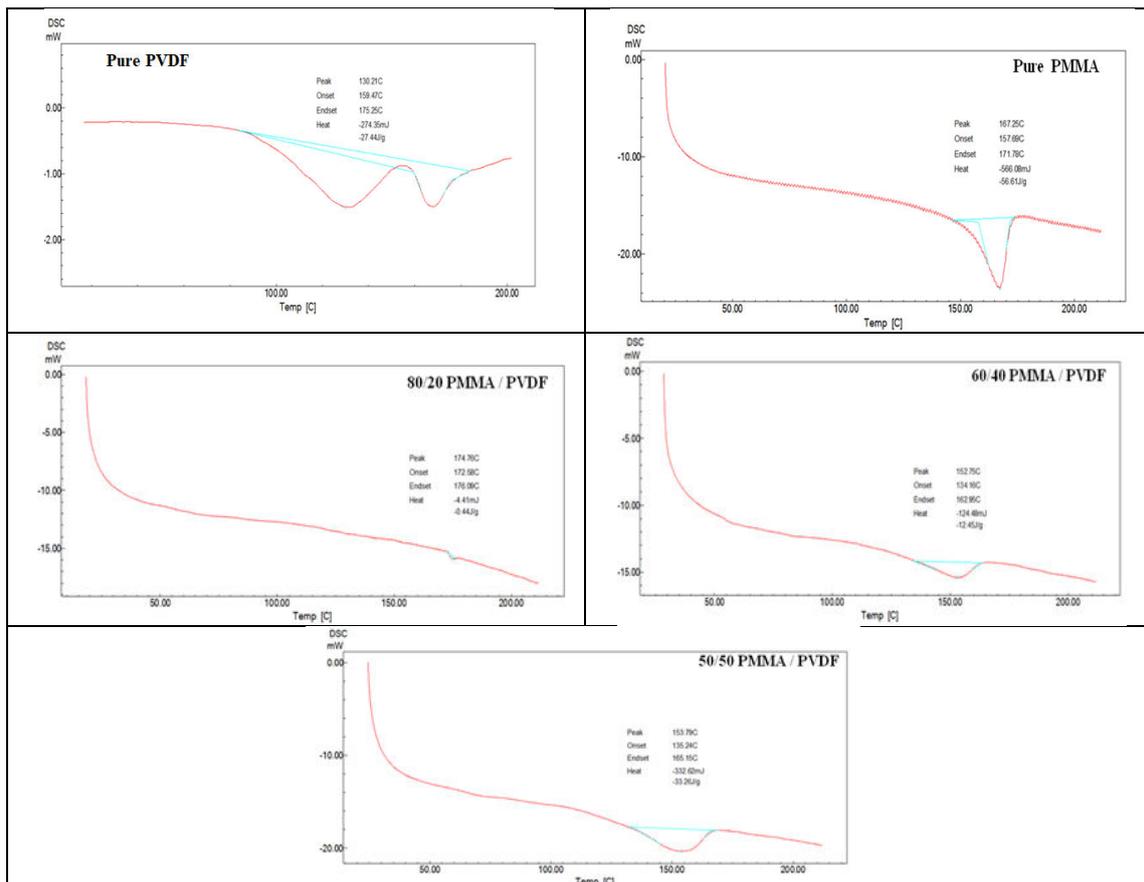


Figure-10. DSC thermograms of (PMMA/PVDF) polymer blend.

#### 4.4 Electrical conductivity

The direct current D.C. of composites was estimated by utilizing Equation. (9). Figure-11 shows the variation of direct current D.C. of (PMMA/PVDF) blend with weight percentage of PVDF at 90 °. With the increasing PVDF concentrations, D.C. electrical conductivity of (PMMA/PVDF) blend increased and significantly increased at 50 wt. % concentration of PVDF. Because of the expansion in the charges bearers number, electrical conductivity was increased with increasing PVDF concentrations [22]. Also, the  $\alpha$  to  $\beta$  change in PVDF provoke free ionic charges in the composite which caused to the expansion in the quantity of the charge transporters, so increment the conductivity [23].

Figure-11 clarified the influence of annealing temperature on the D.C. electrical conductivity of (PMMA/PVDF) blends.

The electrical conductivity for all specimens was increased which is credited to increase the portability and number of charge transporters inside the (PMMA/PVDF) blends[22,24] where PVDF chains can serve as traps for the moving charge bearers by the process of mobility, the strengthening temperature grant ability of movement for the polymers chains and released the trapped charges.

In this way, the increase of current in (PMMA/PVDF) composites is due to two parameters: mobility and number of charge carriers [22].

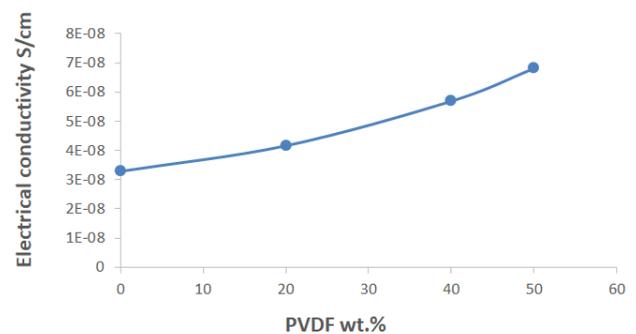


Figure-11. Variation of D.C electrical conductivity as a function of PVDF content of PMMA/PVDF polymer blend.

#### 5. CONCLUSIONS

- Increasing PVDF concentration caused increasing the absorbance of (PMMA/PVDF) blends and decreasing the transmittance.
- The examined specimens clarify a strong absorption and convey in absorption band edge to a higher (optical) wavelength.
- The current optical window enables used as an optical sensor or bandpass filter in the wavelength 350-420nm in the UV and VIS regions.
- The outcomes of optical conductivity spectra exhibited that the prepared specimens can be



transmittance near infrared region and within visible region.

- e) With increasing the PVDF concentration, the D.C. electrical conductivity of annealed (PMMA/PVDF) mixture was raised.

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