Preparing Medical (Polyvinyl Alcohol-Iodine) As A Pressure Sensor and Investigating Its Physical Properties

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ABSTRACT

In this paper, polyvinyl alcohol-iodine (PVA: I2) mixtures were prepared by adding 2, 4 and 6 wt. % of I2 to the PVA matrix. Piezoelectricity, dielectric parameters (D.C conductivity, dielectric constant, dielectric loss, A.C conductivity), X-Ray diffraction (XRD) and Differential Scanning Calorimetry (DSC) were measured. The decisive factor (DF) concept was used to evaluate and specify the types of the destroyers bonds due I2 addition.

Results showed that the D.C conductivity increases with I2 content temperature as well as this conductivity increases with rising temperature up. The dielectric constant decreases with the angular frequency. The A.C conductivity increased with I2 content as well as angular frequency.

I2 addition shifted the crystallinity peak to higher position, decreased the d spacing and increased the crystallite size. DSC analysis showed that the Tg decreased with increasing I2 content followed by decreasing the decisive factor. This analysis also proved that all destroyed bonds due I2 addition are secondary forces type namely, London forces. Composite sample, especially 6 wt. % sample exhibited piezoelectric phenomenon.

Key Words: PVA, Iodine, Film, Activation energy, Piezoelectricity.

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INTRODUCTION

Piezoelectric materials convert energy between mechanical and electrical domains [1]. The necessary condition for the piezoelectric effect is the absence of symmetry center in the crystal structure. This effect is formed in crystals that have no symmetry center. Each molecule in these crystals has a polarization, one end is more negatively charged and the other end is positively charged and is a dipole. The polar axis is an imaginary line that runs through the center of both charges on the molecule. In a monocrystal, the polar axes of all dipoles lie in one direction. The crystal is said to be symmetrical because if the crystal is cut at any point, the resultant polar axes of these two pieces would lie in the same direction as the original.

If the lead zirconate titanate is placed between two electrodes and a pressure causing a reduction of only 1/20th of one millimeter is applied, a 100,000-volt potential is produced.

The basic equations of piezoelectricity are:

$$P = d \times \text{stress}$$
$$\text{and} \quad E = \text{strain} / d$$

Where,
P = Polarization,
E = generated electric field and
d = piezoelectric coefficient in meters per volt.

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Piezoelectric materials may be natural (quartz, Rochelle salt, topaz, silk, wood, enamel, dentin, bone, hair) or man-made (crystals that are quartz analogs, ceramics, polymers and composites). Only 20 of the 32 crystal classes allow piezoelectric properties [2]. Ten of these classes are polar, i.e. they show a spontaneous polarization without mechanical stress due to a non-vanishing electric dipole moment associated with their unit cell. The remaining 10 classes are not polar, i.e. polarization appears only after applying a mechanical load [3].

Traditional ceramics such as quartz, lead zirconate titanate (PZT), and Barium titanate show good piezoelectric property, but it cannot be used in biomedical applications due to its rigid and high acoustic impedance characteristics of piezoelectric crystals. However, polymers like Poly vinyl carbonate (PVC), Nylon 11, and polyvinylidene fluoride (PVDF) also show piezoelectricity and are light weight and flexible [1].

Transient pressure measurement used to study explosives, combustion engine (knock sensors) and any other vibrations, accelerations, or impacts.

Electrical conduction is the process of electric charges transfer through a medium from one place to another under the influence of electric field. Electrical conduction depends on two factors: First, the type of charge carriers (n).It can be electrons, holes or ions automatically generated due to the addition of impurities. The second is the mobility (μ), which depends on temperature (T) and the applied potential (V)."

Polymers of special structure (alternating) have the properties of semiconductors, whereas most commercial polymers are insulator. Given that polymers are easily formed, chemists and physicists started to develop conductor polymers characterized by alternating double bonds since mid the twentieth century"

In its stable state, alternating polymers are insulators or semiconductors because it is not easy for electrons to transfer from one chain to another. These insulator polymers can be transformed into conductors by adding small molecules (impurities or dopants) by doping process. Dopants can operate as oxidizing or reducing factors. Charge transfer complexes can be created between dopants and polymers that make these polymers conductors [4].

The D.C electrical conductivity of polymers depends on the free ions, which are not chemically connected to the large molecules [5]. Polarization can be electronic, ionic, orientation and interfacial type.

Electronic Polarization (P_e) occurs due to distortion in the distribution of the charge as a result of an external electrical field. A separation occurs between the nucleus positive charge and the center of the negative charge, which results in generating induced dipoles; this takes place in a very short time (10^{-15}s) and is independent on temperature [6].

Ionic Polarization (P_i) was formed in an ionic compound having ionic characteristics. It takes place when the matter is under an electric field, which changes the ionic bond lengths resulting in the generation of a net dipole moment that has not been existed in the molecule before. It lasts for a short time (10^{-13} - 10^{-11} s). This type of polarization is independent on temperature.

Rotational or Orientation Polarization (P_d) happens in molecules having permanent dipole moment. On applying an electric field, the dipoles revolve around the axis and arrange in the field direction. This type of polarization depends on temperature, and takes a considerable time to occur [7].

Space Charge or Interfacial Polarization (P_0) takes place when a matter contains impurities, vacuum or structural flaw resulting in the concentration of opposite charge on the impurity terminals; this means the generating of dipoles in the atom, molecule or region of the matter. This type of polarization depends on the homogeneity of the matter and the rate of being free from impurities. It mostly takes place in radio waves and can extend to below audio frequencies depending on the flaw causing the polarization [8].

The energy gap (E_g) is very much greater in insulators than in conductors and semiconductors; and the conduction band is empty of electrons, which are distributed in insulators at lower energy levels of the valence band, making them strongly bound to the atom with little movement. To be released, these electrons require high energy to be enable to transfer to a higher energy level, weaken their binding to the atom, and facilitate their movement among atoms [4].

2. Experimental part

2.1 Materials

Poly (vinyl alcohol) was purchased from Verdean house, Daryaganj, New Delhi-110002 (India) with the degree of hydrolysis (86.0 -89.0 %) and molecular weight of 85,000 g / mole.

Iodine purchased from Merck (Darmstadt, Germany) with the density at 20°C is 4.93 g.cm^{-3} and melting point is 114 °C.

2.2 P reparation of PVA/I_2 film

PVA/Iodine films were prepared by mixing PVA solution with I_2 solution. PVA solution was prepared by dissolving (1g) PVA powder in 40 ml distilled water (DW) with continuous stirring for 15 min in 70°C . I_2 solution was prepared by grinding the iodine molecules, adding I_2 powder to DW by 2, 4and 6 wt. % ratios and leaving these solutions for three hours in sealed glass container at the room temperature.

2.3 Tests

HIOKI 3532-50 Hi TESTER used to measure the dielectric parameters, SHIMADZU DIFFRACTO meter XDR – 6000, LABX used to evaluate the crystallite behavior, SHIMADZU DSC-60 used to measure T_g and Electrometer (Keitthely)(type2400) 60-200 bar used to investigate the piezoelectric tendency.

3. Results and Discussion

3.1 Piezoelectric Results

Figure 1 shows the effect of pressure on the electrical resistance of the prepared samples. It is clear that the electrical resistance of these samples were affected by changing the applied pressure. It means that these samples exhibited piezoelectric phenomena, especially the 6 wt.% mixture.

This piezoelectric mixture has a crystalline region with an internal dipole moment. These dipole moments are randomly oriented without any mechanical or electrical poling process, and in this condition, the net dipole moment is zero and has no piezoelectric response [2]. But, with post processes such as mechanical stretching and a high electric field, crystalline regions inside the bulk film will align in electric field direction [2].

When an electric field is applied to a piezoelectric material, deformation (D_L) or strain (D_L/L) arises. When the field alternates, mechanical vibration occures, and if the drive frequency is adjusted to a mechanical resonance frequency of the device, a large resonating strain is generated. This phenomenon can be understood as a strain amplification due to accumulating input energy with time (amplification in terms of time), and is called piezoelectric resonance. The amplification factor is proportional to the mechanical quality factor *QM*. Piezoelectric resonance is very useful for realizing energy trap devices, actuators, etc. [3].

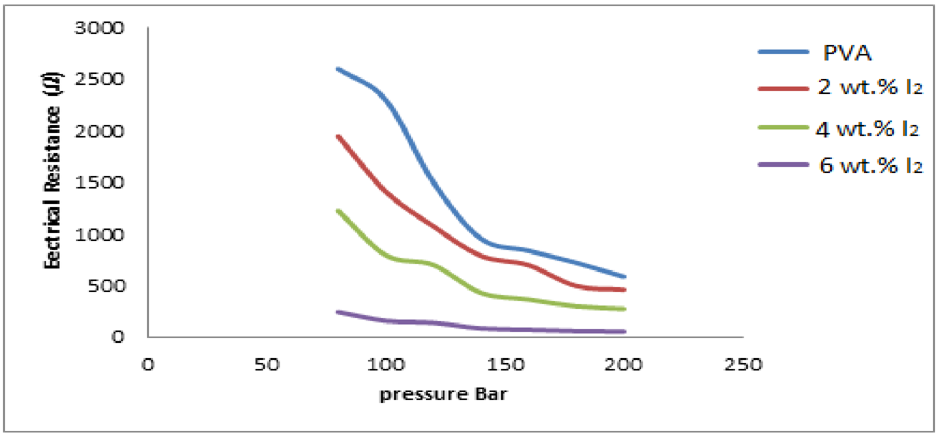


Fig. 1: piezoelectric behavior of pure PVA and PVA: I_2 mixtures

3.2 Electrical measurements

Figure 2 shows the relationship between volume electrical conductivity of (PVA: I_2) mixtures with the temperature.

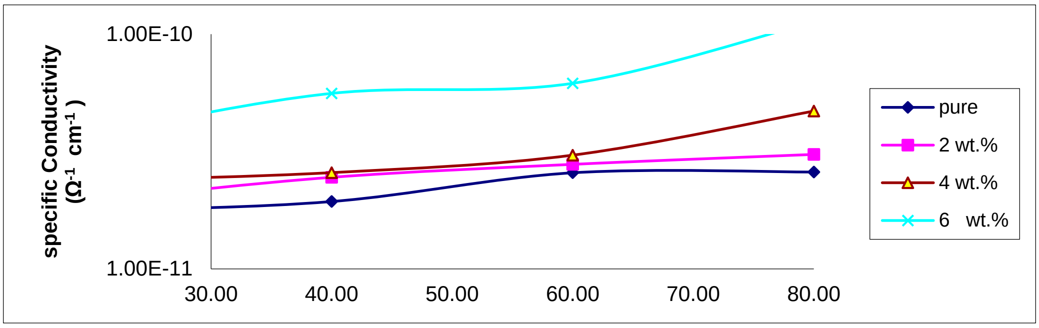


Fig.2: D.C electrical conductivity with temperature of (PVA: I_2) mixtures

It is clear that conductivity increased for any certain temperature with rising iodine concentration. The reason is that the high charge carriers increase linearly with the surging filler content [10].

Ordinary, electrical conductivity increases as a function of temperature due to rising the energy of the conductive electron and enhance its transition to the conduction band.

Figure 3 shows the variation of the dielectric constant of PVA: I_2 composites with angular frequencies.

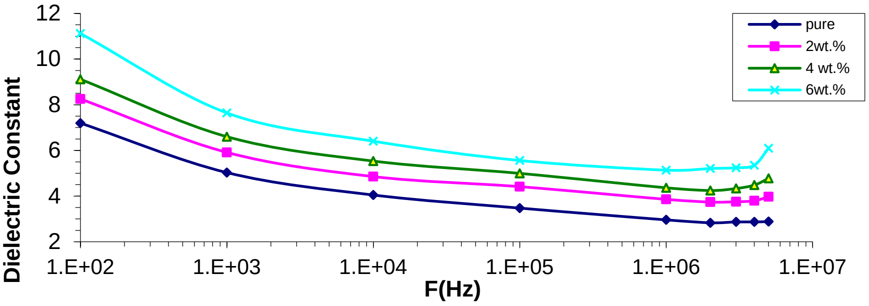


Fig. 3: Variation of the dielectric constant of PVA:I_2 mixtures with angular frequency

The dielectric constant values decreased with enhancing applied frequency. The high frequencies result in decreasing space charge polarization to the total polarization. The space charge polarization becomes more contributing type of polarization at low frequencies, and less contributing with the increase of frequency, this would result in decreasing dielectric constant values with the increase of frequency up to 1×10^7 Hz. The other types of polarizations appear at subsequent frequencies. The ionic polarization reacts slightly to the variation in the field frequencies compared with electronic polarization; this is because the mass of ion is greater than that of the electron. The electrons respond to even high frequencies of the field vibrations. The low mass of electron makes the electronic polarization the only type of it at higher frequencies; this makes the dielectric constant approximately stable for all samples at high frequencies [11].

Figure 4 shows the dielectric loss of PVA: I_2 mixtures. It is clear that the dielectric loss increase linearly with I_2 concentration. This is due to the created voids of iodine sublimation.

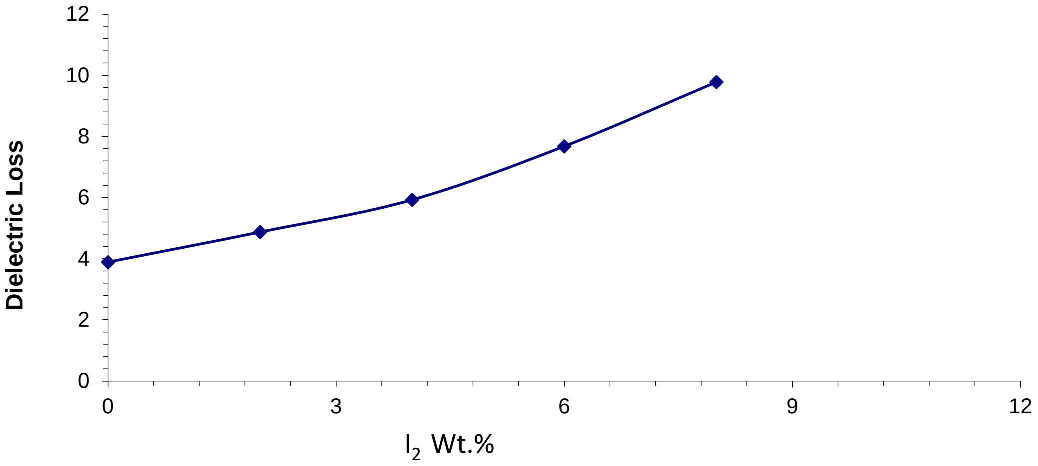


Fig. 4: Dielectric loss as a function of I2 concentration

Figure 5 shows the dielectric loss as a function of the angular Frequency.

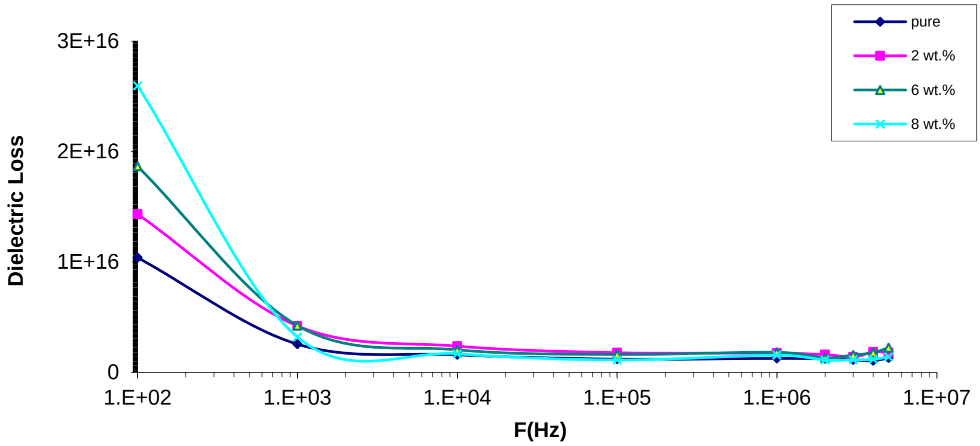


Fig. 5 : Dielectric loss as a function of the angular frequency

The dielectric loss decreased firstly that is the lowest absorption of applied field. This absorption happens due to Maxwell - Wagner phenomenon that is caused by A.C current from the difference of dielectric constant and conductivity of the phases in the composite. When the frequency (f) increases, the dielectric loss is approximately constant. This is attributed to the mechanisms of other types of polarization that occurs at high frequencies [12].

Figure 6 shows the A.C conductivity of (PVA: I2) mixtures with iodine concentration at 50 Hz and 25oC. The A.C conductivity increased with enhancing iodine concentrations. This increase is due to the effect of the space charge polarization. The ions of iodine take the form of clusters or separated groups. This increase is in the result of high ionic charge carriers and formation of a continuous network of iodine ions inside the mixture. Consequently, the conductivity is increasing with rising iodine concentration [13].

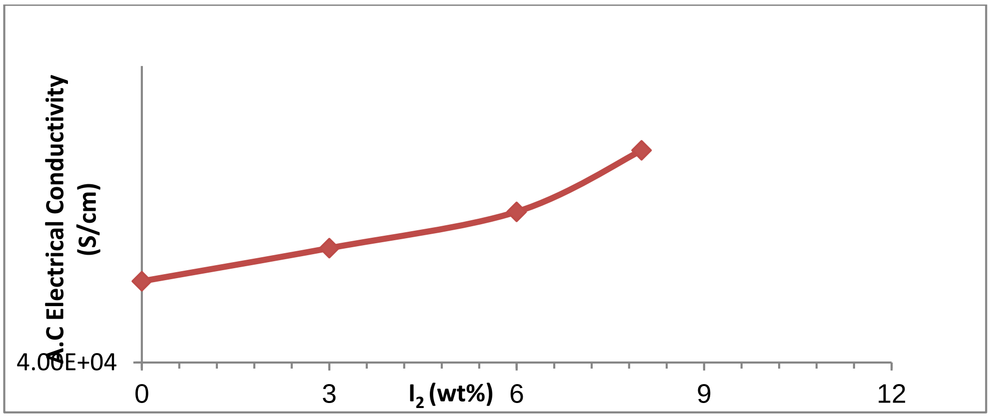


Fig. 6 : The A.C conductivity of (PVA: I_2) mixtures with I_2 content

3.3 X-Ray Results:

Figure 7 shows the crystallinity behavior of pure PVA and for PVA: I_2 mixture with 6 wt.% I_2.

It is clear from table 1 that I_2 addition increase the position of the general peak from 2θ =17.6089 deg to 20.9003 deg. The reason is that iodine is a crystalline element and extends the theta value, thus the space between the planes will be decreased according to Brag law $(n\lambda = 2d\sin\theta)$. This is in agreement with changing the value of d-spacing from $5.03258A^{\circ}$ to $4.24689A^{\circ}$

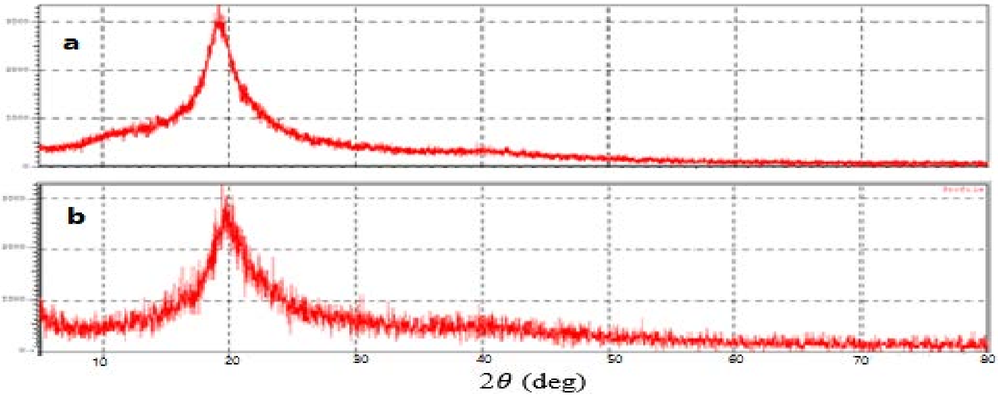


Fig. 7 : XRD pattern for (a) pure PVA and (b) 6wt.% mixture

According to Scherer's equation $\left(size = \frac{k.\lambda}{\beta\cos\theta}\right)$, the crystallite size increased from 5.535 nm for pure PVA to 7.03696 nm for mixture with 6wt.% I2.

In this calculation k (shape factor) taken as 0.89 and λ is x-ray wavelength equal to $1.5418\,A^{\circ}$. The following equation was used to convert from degree to radius.

$$R = \frac{\pi D}{180}$$

Where D is degrees, R is radius, $\pi = 3.14$

1-Pure PVA

$$\Theta \text{ in radius} = \frac{\pi\, 8.80445}{180} = 0.7853975$$

Converting β from degrees to radius $: \beta = \frac{\pi\, 1.6}{180} = 0.027952268$

$size = \frac{k.\lambda}{\beta\cos\theta}$ (Scherer's equation)

$$\therefore size = \frac{0.89 * 1.5418}{0.02795226 * \cos(0.7853975)} = 55.35A^{\circ}$$

$$= 5.535 \text{ nm}$$

$$= \frac{\mathbf{2\cos(0.7853975)}}{\mathbf{1.5418}} = 1.2970632377$$

2. By addition 6 wt.% I_2 to PVA :

Repeat the same calculations but for 2θ = 20.9003 deg, β = 1.12 deg and d-spacing = 4.24689 A° , results shown in table (1).

Table 1:XRD Parameters for pure PVA and 6wt.% mixture

Sample	2θ (deg)	θ (rad)	d-spacing (A°)	β (deg)	β (rad)	Scattering function
0%	17.6089	0.7853975	5.03256	1.6	0.02795226	1.2970632377
6%	20.9003	0.1823894	4.24689	1.12	0.0195377778	1.2970509981

Scattering functions for the pure PVA and the 6 wt% mixture were calculated from the following equation:

Scattering function $=\frac{2\cos\theta}{\lambda}$

and the results were shown in table 2, which indicate the slightly decreasing in scattering function due to the increasing in the crystallinity.

Table 2: Scattering functions for pure PVA and 6 wt.% mixture

Sample	Scattering function
0	1.2970632373
6 wt%	1.2970509981

3.4DSCResults

Figure8shows the DCS analysis of pure PVA and (PVA:I_2) mixtures. The activation can be calculated as follows:

$E_a = \Delta H‡ + RT$ [14]

Where:

E_a: activation energy (kJmol^{-1}), ΔH‡: activation enthalpy (kJ mol^{-1}),

RT: thermal energy (work); RT=P dV(kJ mol^{-1}).

According to molecular models (the activation energy for chain rupture is about 60 kCal/mol (251 kJ mol-1), so that at room temperature the value of the decisive factor for chain rupture as a thermal fluctuation process is about 101[15].

$\therefore E_a = \Delta H‡ + RT = RTD_f$

Where:

R:the gas constant ($0.0083\ \text{kJ K}^{-1}\ \text{mol}^{-1}$)

T: the absolute temperature (K)

D_f:decisive factor E_a at R.T=251 kJ mol^{-1}

$E_a = \Delta H‡ + RT = 251$

Since RT value small at room temperature which is equal to 2.47 kJ mol^{-1} comparing with ΔH‡:

$\because \Delta H‡ \gg RT$

$\therefore E_a = \Delta H‡ = RT\, D_f$

$E_a = 0.0083\ \text{kJ K}^{-1}\ \text{mol}^{-1} * 298.15$

$\text{K} * D_f = 251\ \text{kJ mol}^{-1}$

$D_f = 101.43$

Each unit of $D_f = \frac{251}{101.43} = 2.475\ \text{kJ mol}^{-1}$

1. Pure PVA

T_g of pure PVA= 95.57 ℃ (from fig a)

$E_a = RT\, D_f$

$251 = 0.0083 * 368.57 * D_f \rightarrow \quad D_f = 82.049$

$\Delta D_f = D_f$ at R.T$-$ D_f at 95.57 ℃

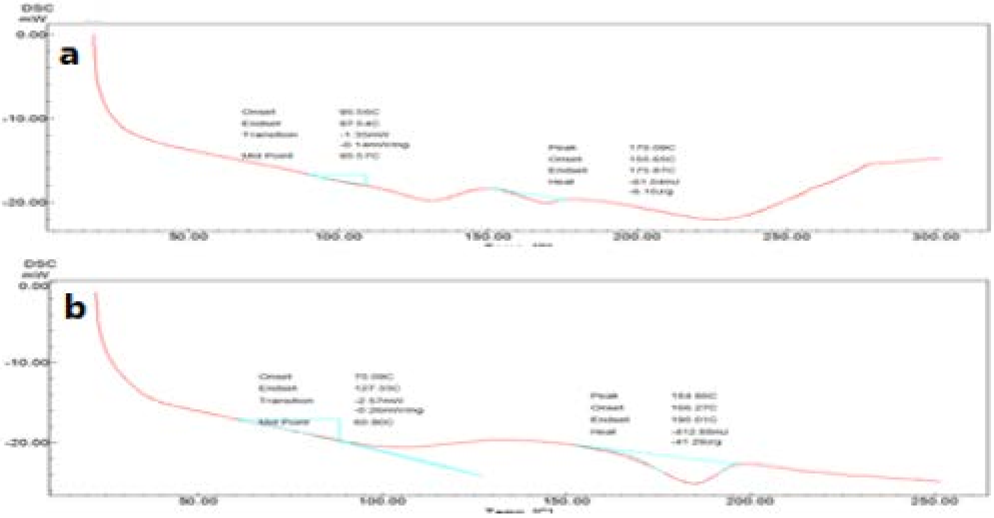
$= 101.43 - 82.049 = 19.38$

Addition E_a from different temperatures (25 to 95.57°C):

$= \Delta D_f *$ Each unit of $D_f = 19.38 * 2.475 = 47.718$ kJ mol^{-1}

E_a (at 95.57°C) = 251$-$ 47.718 = 203 kJ mol^{-1}

$\Delta T = 95.57 - 25 = 70.57$ ℃



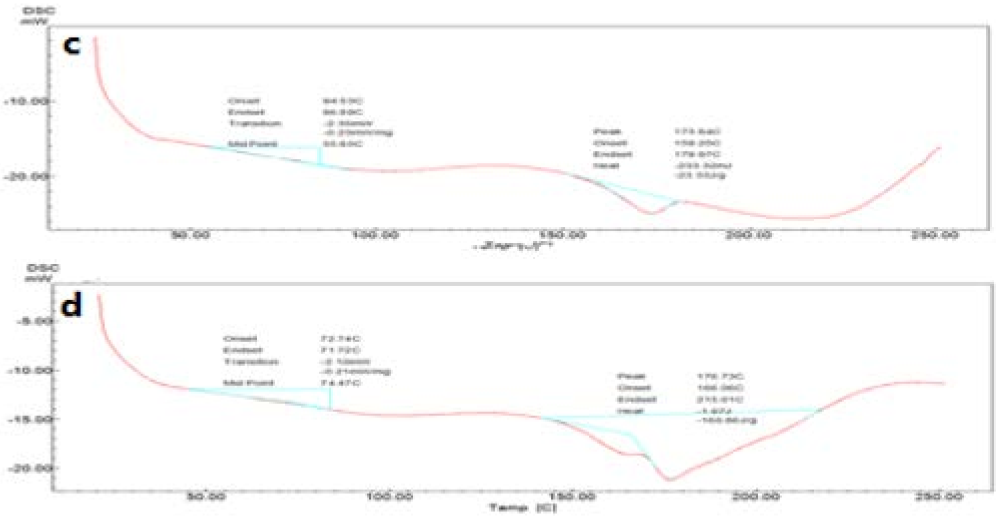


Fig.8: DSC curves for (a) pure PVA (b) 2 wt.% mixture (c) 4 wt.% mixture (d) 6 wt.% mixture

$$1°C = \frac{addition\ Ea}{\Delta T} = \frac{203}{70.57} = \text{kJ mol}^{-1}$$

2. For 2wt.% composite

The temperature of chain rupture falls to 60.9°C due to addition 2%$I_2$to the PVA (Figure b)

$\therefore T_g$= 60.90°C

E_a=RTD_f

251=0.0083∗333.9∗D_f →D_f=90.569

ΔT= 60.9−25=35.9°C

Addition E_a from different temperatures from 25 to 60.9 °C:

=35.9°C∗0.679 kJmol^{-1}°C =24.3761

Given energy by I_2 addition= 47.718−24.3761

= 23.5907 kJ mol^{-1} (this given by 2wt.% I_2)

E_a (at 60.9 °C) =203-23.5907= 179.4093 kJ mol^{-1}

3. For 4 wt.% composite

The $T_g$falls to 55.85 °C due to addition 4% I_2 (Figure c)

$\therefore T_g$=55.86°C

Repeat the samecalculations forT_g= 55.85°C, result shows in table 2.

4. For 6 wt.% composite

The temperature of chain rupture falls to 50 °C due to addition of 6wt% of I_2(figure d).$\therefore T_g$ = 50 °C

Repeat the same calculations for T_g=50°C(table2).

Results are arranged in table 2, and compared with the value of energies of the secondary bonds (table 3). This indicates that the types of destroyed bonds due to I2 addition are Van der Waals bonds and Dispersion (London) forces.

Table 2: Effect ofI2 on PVA at R.T&Ea (251 kJ mol-1) with Df= 101.43

Sample	T_g (°C)	D_f	E_a at T_g (kJ mol^{-1})	Addition E_a (kJ mol^{-1})
Pure PVA	95.57	82.049	203	47.718
2wt% I_2	60.90	90.569	179.40	24.3761
4wt% I_2	55.85	91	153.020	20.94715
6wt% I_2	50	93.63	149.082	16.975

Table 3: Expected destroyed secondary bond by Iodine in PVA.

Sample	Given energy by addition pigment (kJ mol-1)	Secondary bond energy[4] (kJ mol^{-1})	Expected type of destroyed bond
2wt% I_2	23.5907	0.08-40	(Van der Waals bonds) Dispersion(London) forces
4wt% I_2	27.01965		
6wt% I_2	30.9918		

Conclusion :

1-D.C conductivity increased with I_2 content temperature as well as this conductivity increased with increasing temp.
2-the dielectric constant decreases with the angular frequency.
3-The A.C conductivity increased with I_2 content as well as with angular frequency. 4-Decreasing the d-spacing and increasing the crystallite size.
5- The T_g decreased with increasing I_2 content followed by decreasing the decisive factor.
6- Composite sample, especially 6 wt.% sample exhibited peizoelectrical phenomenon.

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