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Verification of the Changes in the Structural and Optical Properties of PVA/PEO Embedded by Lithium Chloride.

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ABSTRACT

Polyethylene oxide (PEO) and polyvinyl alcohol (PVA) were blended and the blend doped with various concentrations of Li Cl using casting method. Verifications of the changes in the structural, optical, thermal and electrical properties are studied FT-IR analysis is confirmed the complexation between the blends and Li-ion. The change in the intensity with shift of IR- bands indicates that an interaction and compatibility between PVA/PEO with LiCl takes place. The UV-Vis spectra suggested presence of a band gap which depends on the LiCl concentrations. The absorption intensity for the samples doped with LiCl become faint lower than pure blend. The peak position at 370 nm is shifted toward higher wavelengths with increasing of LiCl indicates that formation of hydrogen bonds between Li-ions and OH groups that are in consistence with IR results. The values of energy gap for direct and indirect transition decreases with increase of LiCl indicate to presence of charge transfer between PVA/PEO and LiCl. The TGA curves for all the samples have the same behavior with more steps of decomposition of the samples are observed. The reduction of mass loss for the samples contains LiCl compared to pure blend due to crosslink formation. The values of DC conductivity are modified and improved suggest that this system can be used in rechargeable lithium batteries.

Keywords: Blend; FT-IR; UV-Vis; Thermal properties; DC conductivity

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INTRODUCTION

Polymer and/or polymer blends play an important role in wide applications because of their simple synthesis in pure form or with filler and diverse resulting in physical properties [1]. Blends with modifications and improvements in the properties are produced by blending between two or more polymers in order to enhancement of their properties [2].

Polyvinyl alcohol (PVA) is used in wide range of industrial sector applications depending on its degree of hydrolysis, molecular weight, tendency to hydrogen bond and blended with other polymers and depending on the filler used [3, 4]. It has high of dielectric constant and charge capacity. The electrical and optical properties of PVA depend on the type and amount of doped filler [5].

Poly (ethylene oxide) (PEO) have a simple chains with enteric linkages, but PVA have a backbone carbon chains and hydroxyl (OH) groups linked with methane groups. Hydroxyl (OH) group are sources of hydrogen bonds (H-bonds) and then of assistance best formation of the blends between the polymers [6]. Trends to synthesis of composites from polymer or polymer blends consisting of metal halides embedded with blends have attention of scientists in the world. These new materials are include the ability to crystallization of PEO with modified and the enhancement of thermal and electrical properties [7]. The advantages of these materials have higher conductivity with Li-ions numbers. So, it is used in Li- batteries application.

The purpose of the present article is to achieve a deeper insight into the basic physical properties of PVA/PVA blend samples doped with different concentrations of LiCl granules. A systematic investigation on miscibility, thermal stability, structure, morphology and electrical properties are discussed using different tools and techniques.

EXPERIMENTAL WORK

Materials:

Polyvinyl alcohol (PVA) with average molecular weight ≈ 14.000 which was supplied from Merck, Germany and polyethylene oxide (PEO) with molecular weight 90000 supplies from Sigma Aldric, USA were used as a basic polymeric materials. Lithium chloride (LiCl) was purchased from BDH chemicals Ltd Poole Co, England. All chemicals were used as without purification.

Measurement Techniques:

The prepared samples are subjected to FT-IR, UV-Vis, TGA and DC conductivity studies. The single beam Fourier transform-infrared spectrometer (Nicolet iS10, USA) in the range from 4000cm^{-1} to 400cm^{-1} is used for FT-IR measurements. The absorption spectra of UV-Vis were measured in the wavelength region of 200-800 nm using spectrophotometer (UNi CAM UV/Vis Spectrometer, England). Thermo gravimetric analysis (TGA) is used to investigate the thermal behavior of the obtained films by A Perkin-Elmer TGA-7. Small amount from samples (8.4-14gm) was taken for investigate with heating from $30\text{ }^{\circ}\text{C}$ to $550\text{ }^{\circ}\text{C}$ with rate of $10^{\circ}\text{Cmin}^{-1}$ in platinum cell and nitrogen atmosphere. Tester insulation type T M14) was used for DC conductivity analysis.

RESULTS AND DISCUSSION

Fourier Transform Infrared (FT-IR):

Figure (1) shows the FT-IR spectra of PVA, PEO and PVA/PEO blend PVA/PEO (50/50wt. %). The FT-IR spectrum of PVA shows main bands as the following: two vibrational bands at 3345 cm^{-1} and 1430 cm^{-1} are attributed to vibrational stretching and bending modes of hydroxyl groups (OH). The band at 2944 cm^{-1} is assigned to asymmetric stretching of CH_2 group. The vibrational of carboxyl group (C=O) occurs at 1730 cm^{-1} . The IR bands at 1093 cm^{-1} and at 943 cm^{-1} are assigned to C-O stretching of acetyl group present on PVA and to C-C, respectively [8, 9].

The IR spectrum of pure PEO shows the bands as: a broad band centered at 3238cm^{-1} is assigned to OH group. The band at 2811cm^{-1} is due to CH stretching mode. Two bands at 1460cm^{-1} and at 1349cm^{-1} are attributed to CH bending and rocking vibrational mode, respectively. The bands for CH_2 symmetric twisting and C-O-C stretching mode are observed at 1240cm^{-1} and 1108cm^{-1} , respectively. Two bands are observed at 945cm^{-1} and at 843cm^{-1} assigned to CH bending and to C-C stretching mode [10-12].

Figure (2) displays the IR spectra of PVA/PEO blend without and with various concentrations (0.5, 1, 2.5, 5, 7.5 and 10 wt. %) of LiCl as filler. It is clear from the spectra in the blend and the samples after adding LiCl that the intensity of the band at 1730cm^{-1} (C=O) is gradually decreased. The stretching band at 3350cm^{-1} (CH_2) is shifted to 3344cm^{-1} , the band at 1349cm^{-1} (CH_2) was shifted to 1338cm^{-1} . The band at 945cm^{-1} for CH bending is shifted to 964cm^{-1} . The change in the intensity and the shift of the bands indicate that an interaction and compatibility between the polymer blend and LiCl occurs.

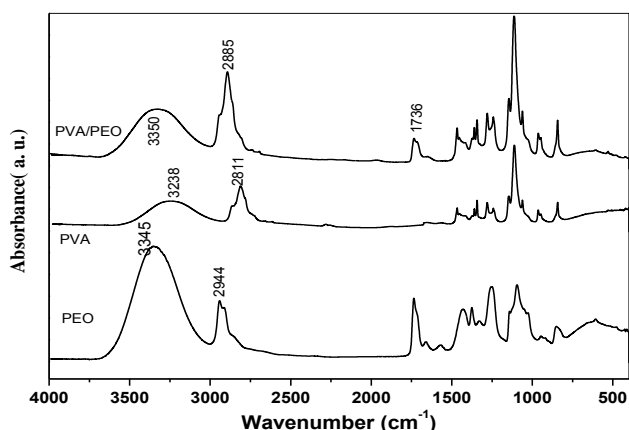


Figure 1: FT-IR spectra of PVA, PEO and PVA/PEO blend.

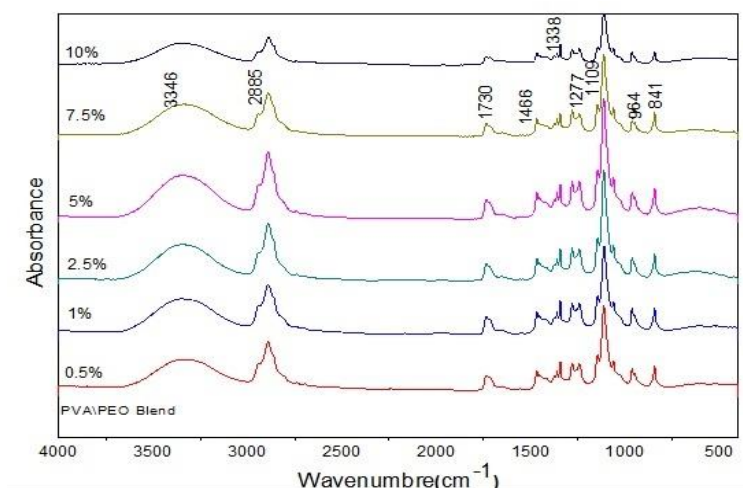


Figure 2: FT-IR spectra of PVA/PEO blend and the blend with various contents of LiCl.

Ultraviolet and visible analysis (UV-Vis):

Figure (3) shows UV-Vis spectra of all films in the range from 190 nm to 1000 nm recorded at room temperature. The spectrum of PVA/PEO blend and the blend filled with various contents of LiCl exhibit small absorbance band in the range from 200 nm to 280 nm.

The PVA/PEO spectrum exhibited three absorption bands, an intense band at 275 nm ascribed to presence of some residual acetate groups of PVA or of existence of carbonyl groups associated with C=O group. A shoulder like hump observed at 340 nm is related to absorption of high energy. The band around 370 nm is due to K-band ($\pi \rightarrow \pi^*$) or to R- band ($n \rightarrow \pi^*$) [13]. Moreover, no presences of absorption bands on the visible range since the samples are transparent.

The intensity of the two bands 275 nm and 340 nm for the samples doped with LiCl become faint lower than pure blend. However, only the peak position of the band at 370 nm is shifted toward higher wavelengths by about 5 nm with increasing of LiCl contents. This shift indicates formation of intermolecular of hydrogen bonds between Li-ions and hydroxyl group (OH) that are in consistence with IR results.

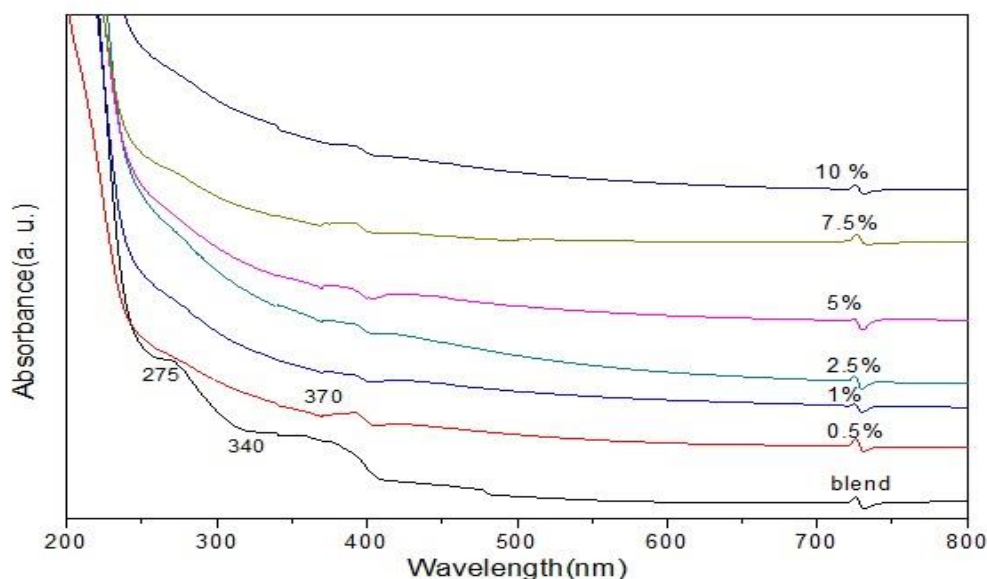


Figure 3: The UV-Vis spectra of PVA, PEO and PVA/PEO polymer blend.

Determination of optical energy gap (Eg):

The UV-Vis absorption edge at low wavelength is one of the most important features of the absorption spectra of crystalline and amorphous materials. The type of optical transition involved in the samples can be obtained from the relation between the absorption coefficient (α) and photon energy ($h\nu$). The estimated values of absorption coefficient (α) can be calculated from absorbance (A) as [14]:

$$I = I_0 \exp(-\alpha x) \Rightarrow \alpha = \frac{2.303}{d} \log\left(\frac{I_0}{I}\right) = \frac{2.303}{d} A \tag{1}$$

where I and I₀ are the intensities of transmitted and incident UV radiation respectively, d and A are the thickness and cross section area of the sample.

The study of optical absorption bands is classified into two kinds: i) direct optical band gap and ii) indirect optical band gap. In direct type, the top of valence and bottom conduction bands both laid at the same zero crystal momentum (wave vector). If the bottom conduction band does not correspond to zero crystal momentum, then it is called indirect band gap (indirect type). In indirect band gap, transition from valence conduction band should always be associated with a phonon of right magnitude of crystal momentum. The basic band edge for both direct and indirect transitions occur and can be observed by plotting $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$, respectively depends on the energy ($h\nu$) from the following equation [15,16]:

$$(\alpha h\nu)^n = h\nu - E_g \tag{2}$$

where $n=2$ and $1/2$, E_g is band gap.

Figures (4, 5) show the plotting of $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ as a function with photon energy ($h\nu$). The linear portions (the intercepts of the energy axis on extrapolating the linear portion of the curves to zero absorption value) in the figures indicate a band energy gap (E_g) in both transitions. At low energy, all spectra in the figure are characterized by presence of an exponentially decay. The values of energy gap for direct and indirect transition are listed in Table (1). The obtained values of E_g decreases with increase LiCl content attributed to presence of Li-ion charge transfer between PVA/PEO and LiCl a filler.

Table 1: Optical energy band gap of PVA/PEO doped with various concentration of LiCl

Sample (wt. %)	E_g (eV) direct method	E_g (eV) indirect method	E_g (eV) Tauc method
0.0	5.27	4.18	4.21
0.5	5.17	3.95	4.09
2.5	5.08	3.72	3.96
5.0	5.00	3.56	3.83
7.5	4.93	3.42	3.65
10	4.85	3.34	3.47

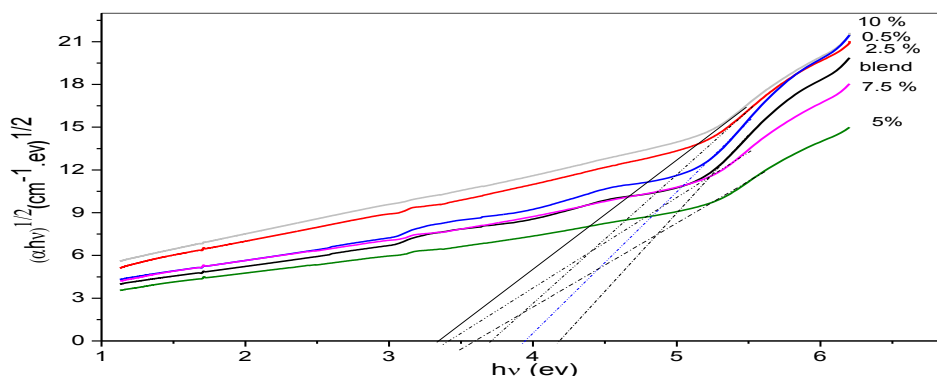


Figure 4: $(\alpha h\nu)^{1/2}$ as a function of $h\nu$ for PVA/PEO blend a with various contents of LiCl.

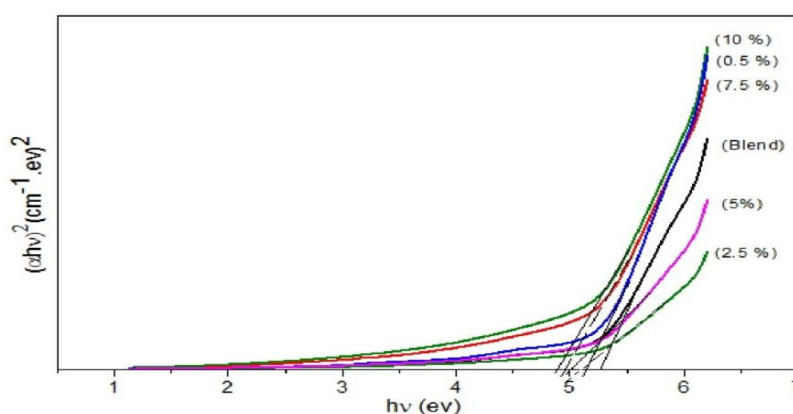


Figure 5: $(\alpha h\nu)^2$ depends of $h\nu$ for PVA/PEO doped with various concentration of LiCl.

Thermo gravimetric Analysis (TGA):

The TGA is a process in a substance is decomposed in the present of heat which causes some broken inside molecules bonds. TGA play an important role to determine the thermal stability and thermodynamic parameters of the materials.

Figure (6) shows TG thermogram of PVA/PEO blend and the blend with various concentration of LiCl in the temperature from room temperature to 500 °C in nitrogen atmosphere to demonstrate the thermal degradation behavior in nitrogen atmosphere (The nitrogen atmosphere prevents autoxidation). The decomposition steps and percentage weight loss for all investigated samples are represents in Table (2). As observed in the figure that the curves represent the TGA for all the samples have the same behavior. From the figure, more steps of decomposition of the samples are observed.

The first decomposition step in TG curves of percentage weight loss up to 3-3.5 % included to the melting temperature of PEO is attributed to evaporation of moisture and gases in the samples [17, 18]. The second step including the melting point of PVA which cover temperature range of 250 to 325°C have a percentage weight loss up to 30.25 %. The third region in the temperature from 360 °C to 415 °C is due to final decomposition state of the polymer blend.

In the first decomposition step is very broad and faint. Thus, it is not possible to determine the peak temperature correctly. However, the mass loss in this region for the doped samples is higher than for pure PVA/PEO blend which support the previously assumption in IR data that LiCl increase the thermal stability of PVA/PEO. On the other hand for third decomposition step, the PVA/PEO decomposed quickly and lost most of its mass. Besides, the weight losses (high percentage) in third decomposition region are believed due to the degradation of intermolecular and partial breaking of molecular structure of PVA/PEO blend. Also, the reduction of mass loss in this for the samples contains LiCl compared to pure blend may be due to crosslink formation by complexing which offers a high strength of bonding.

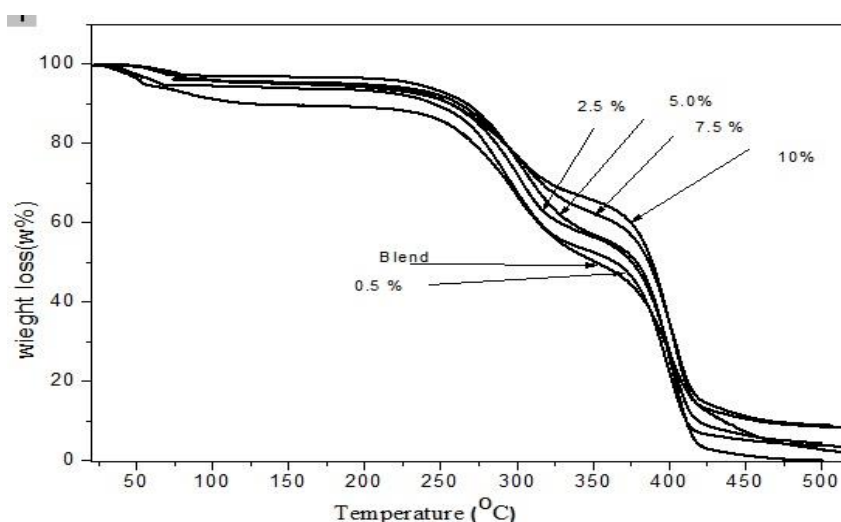


Figure 6: TGA thermograms of weight loss as a function of temperature for PVA/PEO blend with various contents of LiCl.

Table 2: The activation energy for PVA/PEO blend with various contents of LiCl in the second and third region from TGA.

Samples (wt. %)	Activation Energy (K.cal/mole) Second region	Activation Energy (K.cal/mole) Third region
0.0	74.57	126.65
0.5	64.97	117.38
2.5	64.18	114.69
5.0	52.46	108.86
7.5	41.04	95.72
10	39.47	65.30

The general kinetic equation of the decomposition reaction is given as [19]:

$$\frac{d\alpha}{dt} = Af(\alpha)e^{-\frac{E^*}{RT}} \quad (3)$$

where $\alpha = \frac{w_0 - w_t}{w_0 - w_\infty}$ is the fractional reaction, w_0 is initial weight and w_∞ is the weight at the end of final residual mass and w_t is an actual weight at temperature t ; $f(\alpha) = (1 - \alpha)^m$ is the kinetic model function in a differential form; m is the reaction order is the activation energy; R is the gas constant; T is the temperature in Kelvin and A is the pre-exponential factor.

Many methods are used to calculate the activation energy and determine the decomposition mechanisms from TG measurement. In the present, work, Coats – Redfern [20] equation is used for studying thermal degradation kinetics parameters has the following equation:

$$\ln[-\ln(1 - \alpha)/T^2] = \ln[(AR/\phi E^*)(1 - 2RT/E^*)] - \frac{E^*}{RT} \quad (4)$$

where ϕ is the heating rate. The plotting $\ln[-\ln(1 - \alpha)/T^2]$ versus $1000/T$ related to eq.(2) give a straight line. The slopes from the curves give the activation energy ($-E^*/R$).

Figures (7, 8) show the Coats – Red fern relation of all samples in the second and third decomposition steps. The calculated activation energy E^* values for this system in the second and third decomposition regions are given in Table (3) and Table (4), respectively. It is clear that the second composition step showed lower activation energies compared to the third decomposition region. Lower values of E^* are like associated within initiation process which occurred at weakness linkage for composites. At temperature increased, the random scission of the chains between macromolecules is predominated, and then the activation energy has a greater LiCl. This is expected to the increase of amount of LiCl produced. In addition, the joint effect of both elevated temperature and coordination of LiCl are responsible for weakening and strengthening of the composite system.

The activation entropy ΔS^* , the activation enthalpy ΔH^* and the free energy (Gibbs function ΔG^*) are calculated from these equations [21,22]:

$$\Delta S^* = 2.303 \left(\log \frac{Ah}{RT} \right) R \quad (5)$$

$$\Delta H^* = E^* - RT \quad (6)$$

$$\Delta G^* = \Delta H^* - T \Delta S^* \quad (7)$$

where K is Boltzman and h is Planck constant. The entropy ΔS^* gives information about degree of order of system, enthalpy ΔH^* gives information about total thermal energy and Gibbs or free energy ΔG^* gives information about stability of the system.

Table (4) contains the calculated thermodynamics values of ΔS^* , ΔH^* and ΔG^* for the samples in the the third decomposition steps. It is clear that the values of ΔS^* , ΔH^* and ΔG^* for doped samples are less than the values for blend. In addition these thermodynamics values decrease with increasing LiCl. Therefore, it can be concluded that increasing the addition of LiCl to PVA/PEO blend in third decomposition step making them relatively high order, low thermal motion and more thermal stability of such system compared to PVA/PEO blend. This can be discuss as increasing LiCl, the random scission of macromolecule chain in the polymeric matrices predominates and the activation energy has a lower value.

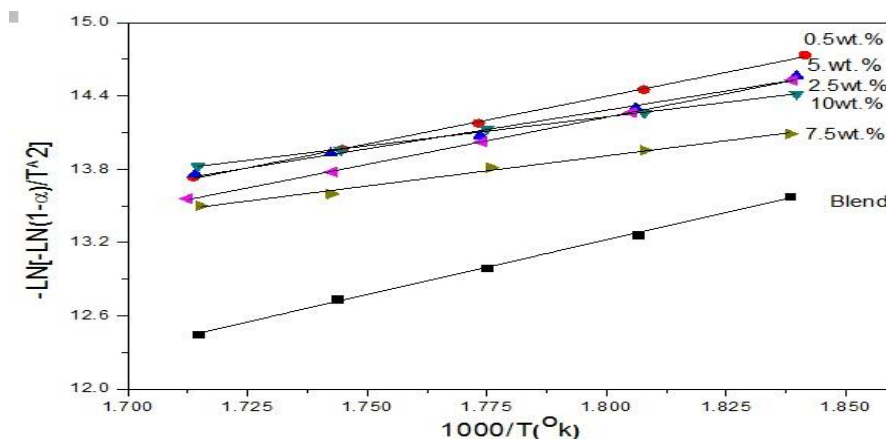


Figure 7: The Coats-Redfern plots of all the samples in the second decomposition step.

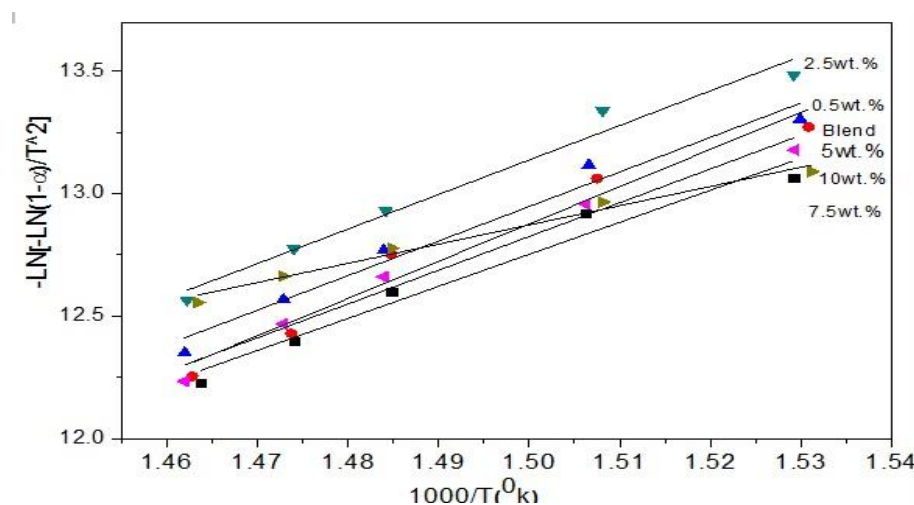


Figure 8: The Coats-Redfern plots of all samples in the third decomposition step.

Table 3: Kinetic parameters and activation energy for PVA/PEO blend and the blend with various concentration of LiCl in the second region.

Samples (wt. %)	Activation Energy Kcal/mole	A	Temp. T _d (°C)	ΔS* k.cal/mole	ΔH* k.cal/mole	ΔG* k.cal/mole
0.0	74.571	4.82	292.4	-137.24	-2356.57	37774.48
0.5	64.97	108.9	304.8	-110.98	-2469.69	31365.4
2.5	64.18	107.6	297.7	-111.28	-2411.78	30728.12
5.0	52.46	1176.2	298.6	-91.377	-2430.65	24859.14
7.5	41.04	7504.1	301.7	-75.88	-2468.01	20431.21
10	39.47	13957.8	298.1	-70.82	-2439.73	18678.18

Table 4: Kinetic parameters and activation energy for PVA/PEO blend and the blend with various concentration of LiCl in the third region.

Samples (wt. %)	Activation Energy Kcal/mole	A	Temp. T _d (°C)	ΔS* k.cal/mole	ΔH* k.cal/mole	ΔG* k.cal/mole
0.0	126.65	0.007	399.1	-188.8	-3190.9	72175.59
0.5	117.38	0.037	400.2	-174.99	-3210.81	66838.18
2.5	115.34	0.045	401.8	-173.33	-3223.98	66434.07
5.0	114.69	0.052	401.8	-172.13	-3226.06	65937.67
7.5	108.86	0.130	400.0	-164.45	-3224.23	62703.12
10	65.30	0.233	400.8	-102.37	-3266.13	37752.16

DC Conductivity Studies (σ_{DC}):

The values of conductivity (σ_{DC}) can be estimated from the general relation:

$$\sigma = \frac{l}{RA} \quad (8)$$

where l is sample thickness, A is surface area and R is resistance which directly measured as relation with increase of temperature.

Figure (9) shows the plots between the variations of $\log(\sigma_{DC})$ various reciprocal absolute temperature ($1000/T$) of the PVA/PEO blend and the blend with various concentration of LiCl. As seen from the figure, if temperature increased, the values of DC conductivity (σ_{DC}) are gradually increased for the samples and the behavior of conductivity does not show any peaks with increasing of temperature. This behavior indicates the amorphous region within the polymer is responsible to conductivity which is related to IR data.

An increase in conductivity can be agreement and explain using the free volume theory [23, 24]. The concept of the free volume theory is: the ionic conductivity is increased for all samples at an increase in temperature due to thermal movement of some segments in the polymeric chains and the dissociation of the fillers would also improve of the conductivity. As increases in the temperature, the amorphous region polymer can be response to expand. The segmental movement in the polymer chain either permits the Li-ions to hop from one site to another or provides a pathway for Li-ions to move easily in amorphous regions. In general, the polymer segments and Li-ions can move to the free volumes and the segmental motion inside the polymer matrices causes facilitates the translational for Li-ionic motion.

The free volume theory of polymeric materials is: an increase in the temperature, the energy of vibration for a segment is sufficient to push against the hydrostatic pressure imposed by its neighboring atoms and create a small amount of space surrounding its own volume in which vibrational motion can occur. So, more of free volumes which produced as temperature increased cause an increase in segments that will assist Li-ion transport and the mobility of Li-ions.

The linearity of the plot in figure (9) suggests that the ionic conduction follows Arrhenius mechanism [25]. The linear behavior suggests the ionic transport which is associated with the polymer chain (i.e., segmental motion).

The results of conductivity can be effectively represented by the following equation:

$$\sigma_{DC} = \sigma_0 e^{-\frac{\Delta E}{kT}} \quad (9)$$

where σ_0 is pre-exponential factor of conductivity related to charge carriers in the samples, E is the activation energy for conductivity of ion transport associated with the configurational entropy of the polymer chains, K the Boltzmann constant and T is absolute temperature.

When $\log(\sigma_{DC})$ is plotted as a function of reciprocal absolute temperature as see in figure, a straight line can be expected with slope $(-E/KT)$ and an intercept is σ_0 . The corresponding values of σ_0 and activation energy E are listed in Table (5). It can be seen gradual decrease in both σ_0 and E are observed with increasing of temperature and concentrations of LiCl.

Moreover, the estimated values of conductivity are increased about three orders from $3.02 \times 10^{-8} \text{ S.cm}^{-1}$ of pure blend to $2.11 \times 10^{-5} \text{ S.cm}^{-1}$ of the sample doped with 10 wt % and at higher temperature. The values of DC conductivity was modified and improved. These results suggest that this system can be used in rechargeable lithium batteries.

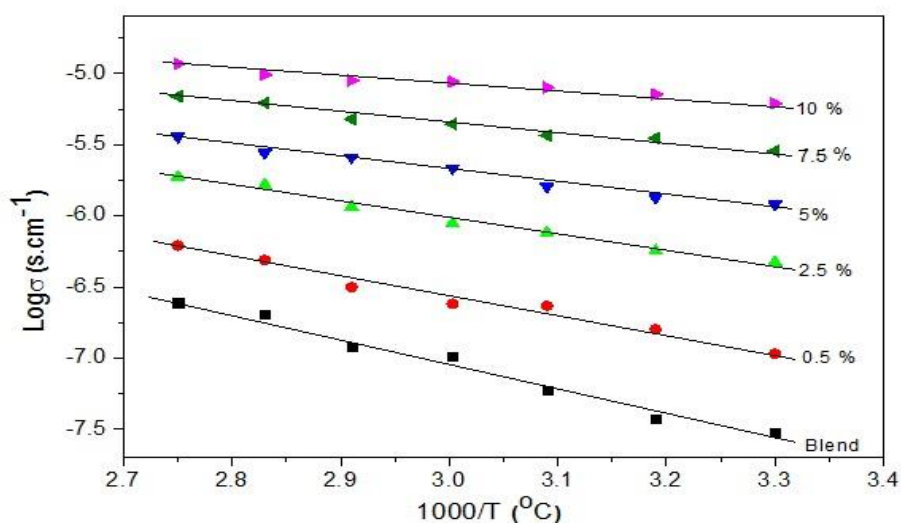


Figure 9: Arrhenius plots of log conductivity versus 1000/T for PVA/PEO blend with LiCl.

Table5: The values of σ_0 and activation energy (E_g).

Samples (wt.%)	σ_0 (S.cm ⁻¹)	E_g (ev)
0	5.96×10^{-7}	0.34
0.5	8.26×10^{-7}	0.25
2.5	2.01×10^{-6}	0.22
5.0	3.09×10^{-6}	0.17
7.5	8.09×10^{-6}	0.134
10	1.16×10^{-5}	0.089

CONCLUSIONS

Verification of the changes in the structural and optical properties of PVA/PEO blend incorporated with various contents of LiCl were prepared and studied using FT-IR, UV-Vis, TGA and DC conductivity. IR spectra confirmed the complexation between the polymer and LiCl. Shift of the peak bands indicate an interaction was occurs between the PVA/EO and LiCl. The peak position of the band at 370 nm is shifted toward higher wavelengths with increasing of LiCl concentrations. This shift indicates formation of intermolecular of hydrogen bonding mainly between Li-ions with OH groups that are in consistence with IR results. The estimated values of energy gap decreases with increase LiCl contents. The TGA thermo grams for

all the samples have the same behavior with three steps of decomposition of the samples are observed. It can be concluded that increasing of the addition of LiCl to PVA/PEO blend make high order, low thermal motion and more thermal stability compared to pure PVA/PEO blend due to the random scission of macromolecule chain in the polymeric matrices predominates and the activation energy has lower value. However, DC conductivity was modified and improved suggest that this system can be used in rechargeable lithium batteries.

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