

Preparation of Electrical Conducting Polymer Composites From Polyvinylchloride (PVC) Resin and Studying Some its Electrical Properties

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Abstract:

The D.C electrical and thermoelectrically properties of randomly mixed isolator – electrolyte system as (Al/ PVC – LiF/Al) junction consisting of polyvinyl chloride (PVC)resin reinforced with Lithium Fluoride (LiF) powder were studied.

A comparison is made the properties of (PVC) material with varying percentage of (LiF) powder (0%, 30%, 50%, 80%)to find out the effect of reinforcement of isolator material. The composites dissolving in 10ml form tetraHaedrofloun (THF) and Solution were the castled in Petri dish and Laved it dry in the air, The out coming Sample were disc - Like shape of a diameter of about 3cm and thickness renege between (0.01- 0.018) cm .

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The experimental results show that current and the conductivity of (PVC - LiF) composites increase by three orders of magnititude when the volume fraction (LiF Vol.%) increase and so dose with temperature.

The activation energy of the thermal rate - process of the electrical conductivity is determined and found to decrease with increasing the LiF vol. % content.

We find that this composite has good conductivity, light weight and easily manufactured. These very good ideal characteristics can make the composite very suitable to be used commercially

Key Words: electrical properties, thick polymer films doped with electrolyte and conducting polymer composites .

Introduction:

The electrical properties of polymers in general allow their application as insulating materials because of their high resistivity [1].

The resistivity can in fact cause problems, particularly for hydrophobic polymers in that it leads to a build up of electrical charge. This can prove hazardous in certain powder industries and the transport of inflammable fuels, and it can prove troublesome in the textile spinning industry. When an industrial material is shown to lack exactly the required

properties for an intended use, the first solution for improvement is to attempt to modify its structure or behavior in the desired direction by adding to it some parts of another material that has the missing properties in excess. Since combinations of two or more materials are called composites, it is evident that most of the industrial material that surround, which have been made and chosen for well-defined properties, are composite materials. Nowadays, composite materials are employed in a vast range

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of uses because they offer combinations of properties and a diversity of applications unobtainable with metals, ceramics, or polymers alone.

Electrical conductivity composites have been the subject of continuous interests to the chemists, physicists and materials and device scientists for many years[2]. This interest arises from the idea of being able to combine in a single material the electrical properties of metal (high conductivity) or semiconductor with those of a polymer (mechanical strength, flexibility, lighter weight, low preparation and fabrication costs, high -strength-to-weight ratio, low fabrication temperature, the flexibility of films and could greatly influence design of electronic as well as other high technology products) for instance[3]. These fillers can be mixed into the polymer, as it is extruded or otherwise preprocessed.

One other option is to metalize the polymer surface through vapor deposition or through spraying atomized metal on to the polymer surface[4]. Modification of physical properties of existing polymers could lead to enhancement of the conductivity of particular polymer by several orders of magnitude. The conductive capability of modification polymers makes possible molded resistance heaters without the use of special heating element [5]. The metalized polymer then a conductive surface that can impart a certain degree of Electro Magnetic interference (EMI) and Radio Frequency Interference (RFI) shielding. The protect business machines, automotive and aerospace components, and putters from EMI [4]. They are providing continuous bleed of static charges [5].

Researches in the field of conductive polymers have attracted

considerable attention for more than 20 years.

Polymer - electrolyte composites in general and PVC - electrolyte composites in particular have gained increasing attention in recent years. The possible applications are in the field of high - energy density batteries, Large - area electro chromic devices, recharge bile batteries, and sensors [4,6].

The Electrical properties of polymer have been studied by Baker and Thomas. They studied the effect of the addition of Ag^+ ions to cellulose acetate. The result showed that the addition of ions not only increases conductivity but also increases the glass transition temperature. They studied the activation energy of conduction and the effects of the ionic concentration of the ion on the electrical conductivity [7].

Viscosity and ionic conductivity were carried out on gel electrolytes made of highly amorphous polymer (PMMA) and $(LiClO_4)$ salt. In the composition range comweight%-35W% of (PMMA) in the gel, the ionic conductivity decreases increase. On the other hand a large increase of viscosity is observed leading to a solid adhesive material [8].

Polyvinyl Chloride Films doped with Aliquat Chloride were studied by the A.C impedance and D.C polarization methods. In those studies the measurement of the effect of composition variation and temperature on the conductivity and the capacitance were studied. The conductivity has been found to increase by three orders of magnitude. The membrane conductivity depends on the ionic site density, ionic mobility's and, ion -pairing [9].

Comb-like polymers (CP), based on modified alternating methyl-vinyle ether/maleic anhydride copolymer with oligo- oxethylene side chains and

complexes with Lithium salt to form amorphous polymer-electrolyte, (CP/Salt) complexes, have been prepared by Liming Ding, et.al. These materials showed conductivity up to 10^{-5} (S.cm⁻¹) at room temperature. The temperature dependence of ionic conductivity suggests that the ion transport is controlled by segmental motion of the polymer. The ionic conductivity maximum moves to a higher value when the salt concentration and the temperature increases [7].

Some electrical proper of polycarbonate /PAN-based carbonfiber composite are reported by Ahmed, et. al. Impedance measurements preformed at frequency range of (1Hz-100KHz) on various composite specimens showed frequency, filler concentration and temperature dependence. The observed results are similar to those reported on most dielectric solid material. The loss factor increases with increases filler concentration as a result of enhancement of the electrical conductivity, the observed decrease in the impedance with temperature may be attributed to the tunneling and the polarization current effects [10].

The electrical conducting of thermoplastic/ polyaniline plate was synthesized through oxidation of the thermoplastic plate by Al- Atrakchiyie.

Two method have been to synthesize the composite, unprotonated polyaniline in the composite and protonated polyaniline in the composite methods. The experimental results show that protonated polyaniline in the composite method is better used in order to obtain high conductivity.

The electrical, thermoplastic properties were investigated noticing the effect of changing the amount of the aniline, the concentration of

oxidation agent and the time of impregnating to the oxidation agent.

We find that this composite has ideal conductivity, light weight and easily manufactured. These very good ideal characteristics can the composite very suitable to be used commercially [4].

The physical, mechanical, electrical and thermal properties of adhesive material that prepared from Nitrocellulose (CN) reinforced with graphite particles and aluminum start by Abass.

A comparison is made between the properties of adhesive material with varying percentage of graphite powder (0%, 30%, 50%, 80%) to find out the effect of reinforcement on the adhesive material.

The ability of property an electrical was studied through the measurement of conductivity a function of temperature varying.

The results of comparison have clearly shown that the increasing of content of the filler material (graphite weight) after limit ratio determined (32%) in material prepare lead to yielding the Nitrocellulose (CN) material to concept of granular agglomeration. The mechanical properties decrease when graphite weight ratio increases. Electrical conductivity and flammability increases with graphite weight percentage increases, while the electrical conductivity decreases with increases of temperature [11].

This work aims to synthesize a polymer composite with high electrical conductivity made of cheap, light available materials and can be used in the everyday life.

In this objective we specifically demonstrate how thick composite polymer films with electrical conductivity extending from insulating to semiconducting and conducting can be prepared therefore concerned with

the preparation of (PVC - LiF) composites with several LiF vol.%. This work also includes the effects of LiF vol.%, and temperature on the DC electrical properties of (PVC - LiF) composite as (Al/PVC - LiF/Al) junction.

Theoretical Concepts:-

(Solid Electrolytes):

Solid electrolytes are Solid materials which possess an electric conductivity partly or wholly due to ionic displacements [12].

In these materials, one component of the structure, cationic or anionic, is not confined to specific Lattice sites but is essentially free to move through out the structures in that there are open tunnels or layers through which the mobile ions may move [13].

The conductivity of Solid electrolytes usually depends upon several factors among them, the temperature [14].

(polyvinyl chloride (PVC)):

polyvinyl chloride (PVC) is a linear - chain polymer which have good mechanical properties and certain electrical properties which make PVC polymer as good candidate in the application in evolving high power capacitors, high frequencies because of high dielectric constants and high power factor values. Table [1] gives some of physical properties of PVC polymer[15,16].

Table [1] physical properties of PVC polymer[15],[16].

Properties	PVC
Density	1.49 g/cm ³
Dielectric constant	3.2 at 60Hz
Glass transition Temp	(75-85)°C
Melting point T _m	(160-170)°C
Work function (ev)	4.85±2
Volume resistivity (ΩCm)	10 ¹⁷ at 20°C

(Lithium Fluoride (LiF)):

Lithium Fluoride (LiF), which is one of the Solid electrolytes, have received particular attention for device application owing to their chemical stability from proper mechanical properties. It has a polycrystalline form of alkali halide family and have been classified as ionic conductors [13]. Table [2] gives some of physical properties of (LiF) polymer.

Table [2] physical properties of (LiF)[17].

Form	Simple cubic (Sc)
T _m °C	842°C
Density (g/cm ³)	2.638
σ at T _m (Ω.cm) ⁻¹	2.4×10 ⁻³
σ at 0K (Ω.cm) ⁻¹	6×10 ⁻⁹
Staticdielectric constant (ε _s)	9.3
Work function W(ev)	2.07

(The Electrical Conductivity):

One of the most important electrical characteristics a solid material is the ease with which it transmits an electric current. Ohm's law relates the current (or time rate of charge passage) to the applied voltage V as follows[4]:
 $V = IR \dots\dots (1)$

where R is the volume resistance.

The D.C electrical conductivity is a property of a material which has the Largest Variation in its Value. The range of electrical conductivity observed in materials covers of 25 orders of magnitude [7].

For a body with constant cross section (A) and a thickness (L), Figure (1), the volume resistivity, ρ_v could be written as;

$$\rho_v = \frac{R.A}{L} \dots\dots (2)$$

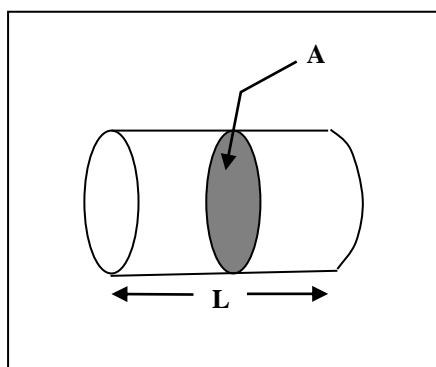


Fig.(1) Determining volume resistivity.

The volume conductivity can be written as;

$$\sigma_v = \frac{1}{\rho_v} \dots\dots\dots (3)$$

$$\text{or } \sigma_v = \frac{L}{R.A} \dots\dots\dots (4)$$

The electrical conductivity for non metallic materials Varies exponentially with temperature (T) according to Arrhenius equation;

$$\sigma = \sigma_o \exp\left(\frac{-E_{ac}}{KT}\right) \dots\dots\dots (5)$$

Where K is the Boltzman constant and E_{ac} is the thermal activation energy.

If the electrical conductivity (σ_v) is measured over a wide range of temperature, the plots of logarithm of the conductivity as function of the reciprocal of the absolute temperature gives straight Lines and from their slopes one can calculate the activation energy, E_{ac} , for thermal process[18].

Materials and Methods:

(Materials):

The PVC polymer, from Intermediate petrochemical Industries Co. Ltd, which is rigid compound Solid in the form of bluish dry mix. It has excelled machine process ability and finished product is transparent and glass powder.

The LiF material is the electrolyte used as a filler in this work, which has a

purity of 99.999% supplied by Ferak company.

(Preparation of Sample):

A weight amount of polymer powder have been mixed with weight amount of LiF powder to obtain different percentages. A tumbling mill has been used to obtain homogenized powder mixture. The polymer samples can be prepared by dissolving (1) gram from polymer and electrolyte composite as the percentage (PVC pure, 70/30, 50/50, and 20/80) for PVC and LiF), table [3] list of weight percentage of (PVC-LiF) specimens.

Table [3] physical properties of(PVC-LiF).

Wt.% PVC	Wt.% of LiF	Vol. % of LiF
100	0	0
70	30	18.09
50	50	34
20	80	67.2

The composites dissolving in 10ml form tetraHaedroflourn (THF) and Solution were the castled in Petri dish and Laved it dry in the air, The out coming Sample were disc - Like shape of a diameter of about 3cm and thickness renegeed between (0.01-0.018) cm .

(Measurement of D.C Resistivity and Conductivity)

A coating unit model (Varian NCR116) has been used for deposition of thin circular aluminum electrode on both sides of each sample. The purpose of these electrode is to minimize the contact resistance and elements the space charge effects. The Three - electrodes method has been used to measure the D.C electrical volume conductivity. Complete description of this technique is found else were stabilized D.C power supply (Phillips Harris Limited) which provides an out put voltage from (0-6kv). The maximum voltage used was (1500) volt. The out put current was measured

by Keithley (616 - digital) Solid - State electrometer of accuracy $\pm(2-4\%)$. The electrometer provides direct reading current ranges to 10^{-15} amperes full scale. The test sample is placed between the two electrodes and left at a desired temperature for about 15 minutes, then the desired test voltage is selected from the voltage supply and the current passing through the bulk of the test sample, at this selected temperature, is measured by the electrometer. This procedure has been repeated twice and the average reading has been taken. The selected voltage is varied from (100-1500) volt, 100 volt each step. The volume resistance has been calculated for each reading and average (R) has been taken. The volume conductivity measurements were performed in the temperature range between (303-373)K by using a temperature controlled oven (Heraeus electronic).

Results and Discussion:-

1. The Effect of LiF Vol.% Concentration on Electrical Volume Conductivity (σ_v).

The variation of volume resistance (R), volume resistivity (ρ_v) and D.C electrical conductivity (σ_v) as a function of the volumetric filler content at a (303K) is shown in figures (2), (3) and (4). The electrical conductivity remains to increase when LiF vol.% content is equal 18.09 vol.%. The figure (4) indicates that increase D.C electrical conductivity for sample of high LiF vol.% content is about three order of magnitude as compared with the D.C electrical conductivity of neat PVC sample. This behavior can be related to the fact that at high filler concentration the electrical properties of composite material may be dominated by the electrical properties of the filler where as at low filler content both polymer and filler govern the electrical

properties of the composite material. The same conclusion has been adopted by other [10]. The electrical conductivity could also be increased as a result of increasing of ionic charge carriers which can be increased due to increasing filler content [19]. The increment in D.C electrical conductivity values of (PVC- LiF) composites can be ascribed mainly to the rearrangement of the electrolyte particles through out the polymer matrix.

The LiF particles are randomly distributed in the matrix as from of network, and when the LiF vol.% is higher, the network starts to connect to each other, to form some kind of conductivity path through the polymer matrix.

The above approach which describes the dependence of the electrical conductivity on the rearrangement of the particles is similar to that observed by other workers [19],[20].

2. Temperature Dependence of D.C Electrical Conductivity.

The effect of temperature on volume resistance (R), volume resistivity (ρ_v) and D.C electrical conductivity of (PVC - LiF) composites shown in figures (5),(6) and (7). The figure (7) shown for all samples of different LiF content (i.e 0 vol.%, 18.09 vol.%, 34 vol. %, 67.2 vol.%), the conductivity increasing with increasing temperature, characteristics of semiconductor material. Further more the value of D.C electrical conductivity has been increased by about three order of magnitude at 373K. This result can be related to the increasing of the ionic charge carriers as well as increasing of polymer segmental motion of temperature increasing.

Several groups of workers have reached a similar conclusion [10,19].

3. The Activation for (PVC – LiF) Composite.

To find the activation energy for thermal activation processes Arrhenius equation (eq.5) have been used and the results have been shown in figure (8). The composites with higher LiF vol.% content have Lower activation energy values. The high activation energy values can be attributed to the thermal movement of ions and the molecules, where as the low activation energy values can be attributed to conduction mechanism which is related to the decreasing of the distance between the LiF particles. Higher LiF content in the PVC matrix mean shorter distances between LiF particle, Figure (9) which shows the decreasing of the activation energy of (PVC – LiF) composites as a result of increasing LiF vol.% content is a reasonable support for the above discussion , it has been reported that for these kind of composites electronic, ionic, as well as mixed conducting processes are possible [8,11].

The range of conducting mechanisms for These composite materials considered from purely ionic to purely electronic including important mixed ionic – electronic cases [9].

Conclusions:-

The main interest in polyelectrolyte can be related to large demand of these material in technological application, for example rechargeable batteries.

A composite material of randomly mixed insulator – electrolyte system as (Al/PVC - LiF/Al) junction consisting of PVC and LiF powder were prepared and found to have several significance D.C electrical properties.

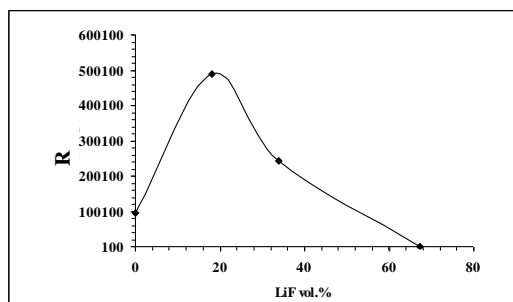


Fig (2) variation of volume resistivity (R_v) with LiF vol.% concentration.

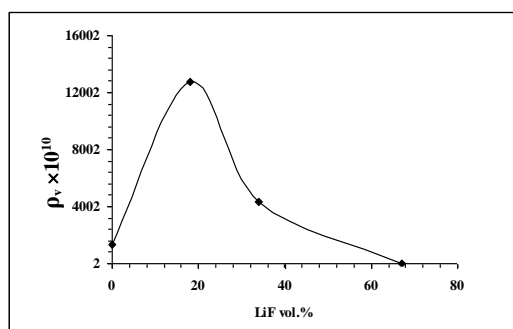


Fig. (3) variation of volume resistivity (ρ_v) with LiF vol.% concentration.

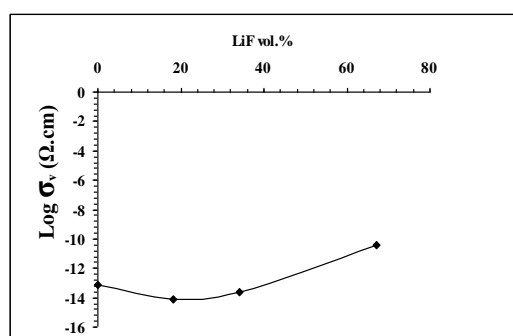


Fig. (4) variation of volume D.C electrical conductivity with LiF vol.% concentration.

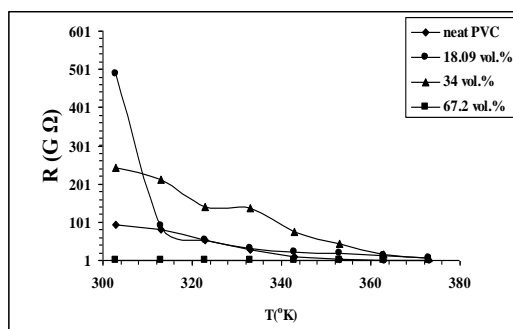


Fig. (5) variation of volume resistivity (R_v) with temperature for (PVC-LiF) composite.

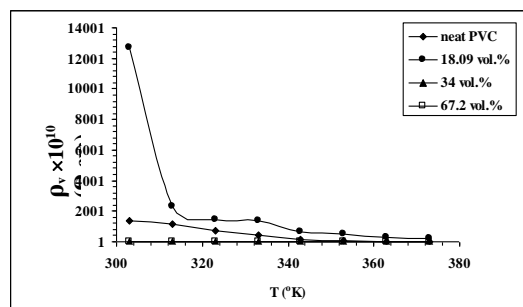


Fig. (6) variation of volume resistivity (ρ_v) with temperature for (PVC-LiF) composite.

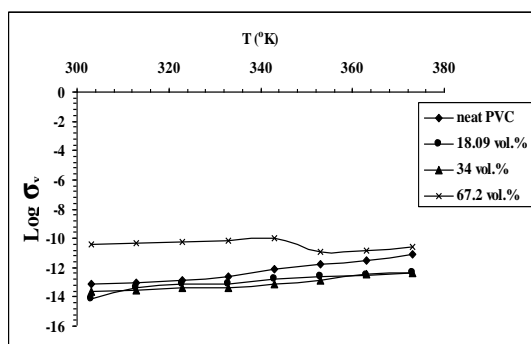


Fig. (7) variation of D.C electrical conductivity (σ_v) with temperature for (PVC-LiF) composite.

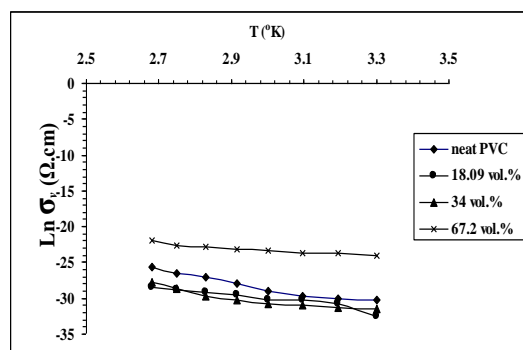


Fig. (8) variation $\text{Ln } \sigma_v$ with reciprocal absolute with temperature for (PVC-LiF) composite.

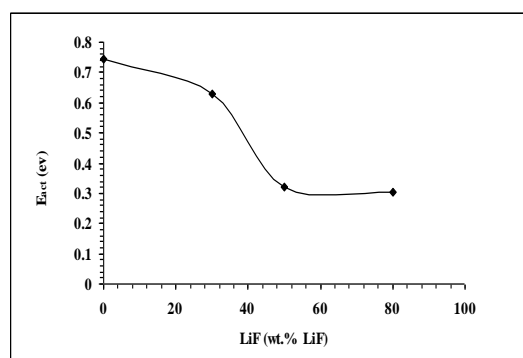


Fig. (9) variation activation energy for D.C electrical conductivity with LiF vol.% concentration.

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تحضير متراكبات بوليمرية من راتنج البولي كلوريد الفانيل (PVC) موصلة كهربائياً ودراسة بعض خصائصها الكهربائية

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الخلاصة:

تم دراسة بعض الخصائص الكهربائية المستمرة والكهروحرارية للخليط العشوائي (بوليمر- الكتروليت) المكون من راتنج بولي كلوريد الفانيل (PVC) (كمادة عازلة) المدعم بمادة فلوريد الليثيوم (كمادة الكتروليتية) والمحضر بشكل مفرق (Al/PVC- LiF/Al), ومن ثم تمت مقارنة خواص هذه المادة المترابطة مع نسب مختلفة من مسحوق فلوريد الليثيوم (LiF) هي (0%, 30%, 50%, 80%) وذلك لملاحظة تأثير التدعيم على المادة العازلة. مع العلم أن سمك النماذج المحضرة يقدر بـ (0.01 - 0.018) cm حيث أمكن الحصول عليه وذلك بذابة هذه المواد المترابطة المحضرة بـ (10ml) من مادة (Tetra Haedro flourn). كما تمت دراسة إمكانية استخدام هذه المادة الرابطة المدعمة بفلوريد الليثيوم في تصنيع مواد مترابطة موصلة كهربائياً عن طريق دراسة التوصيلية الكهربائية عند درجات حرارية مختلفة. لقد أظهرت النتائج التجريبية أن التوصيلية الكهربائية لمترابكات (PVC-LiF) تزداد مع زيادة النسبة الحجمية لفلوريد الليثيوم بمقدار ثلاث مراتب عشرية, كذلك تزداد مع ارتفاع درجة الحرارة كما أن قيم طاقات التشييط تقل بشكل عام مع زيادة النسبة الحجمية لفلوريد الليثيوم المضاف. أن هذه المواد المترابطة تمتلك توصيلية كهربائية جيدة وخفيفة الوزن وسهلة التصنيع وهذه تعتبر ميزات مثالية لصنع مواد مترابطة مناسبة جداً للاستخدام التجاري.