The Study of Dipping Time in Hydrochloric Acid on Electrical Properties of I (PVC-PANI) Blends

Ammar Albaaj
University of Basrah for Oil and Gas

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The Study of Dipping Time in Hydrochloric Acid on Electrical Properties of (PVC-PANI) Blends.

Nadhim A. Abdullah[1] , Hameed A.hamdi[1] and Ammar K .AL-Baaj[2]

[1]Materials Science Department, Polymer Research Center

[2]Chemical Department ,College of Engineer, Basrah University

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Abstract

The electrical properties of polyaniline-polyvinyl chloride blend as a function of dipping time in (5%, 10% v/v) dilution of hydrochloride acid (HCL) are reported using Al/polymer/Al structure while D.C. conductivity is measured by two probes method, the current was measured at steady state condition and the obtained results showed that the domain conduction mechanism was identified as space charge limited current (SCLC) , D.C. conductivity was found to be ($12.3x10^{-8}$ $S.cm^{-1}$) at 5% of HCL dilution and ($8.2x10^{-8}$ $S.cm^{-1}$) at 10% of HCL dilution. The most effective dipping time was (15, 30) minutes for 5% and 10% HCL dilution respectively, and dark D.C. bulk conductivity of the blend was observed to increase by 15 times of it's magnitude in the investigated dipping time meaning less effect of HCL dilution on D.C. conductivity.

Introduction

Although each class of polymer has its own specific properties, there is one feature that almost all polymers seen to have in common they are electrical insulator. These polymers such as PVC and polyamides have been used and continue to be used as materials that surround the copper in electrical wires or that prevent shorts in electrical circuits, there is however, one class of polymers that form an exception to this rule, and they are the electrically conductive polymers. In contrast to other polymers, conductive polymers have the ability to conduct electricity, just like metals such as copper and iron [(1)]. Conductive polymers are generally considered as a relatively young class of polymers, since the first synthesis of such polymers dated back to the first half of nineteenth century[(2)]. Many of these conducting polymers have an array of potential application in the micro electronics industry and optoelectronics devices such as diodes [(3)], field effect transistor[(4)] , light emitting diodes[(5)], photovoltaic cells[(6)],rechargeable batteries[(7)], electrical capacitance[(8)] and sensors[(9-10)]. One of these polymers is polyaniline, this polymer has stand out due to its properties [(11)].

Recently polyaniline has many compounds and blends and also it has many derivatives, which can be designed to achieve the required conductivity for a given application, the resultant blends can be as conductive as a silicon and germanium or as insulating as glass opening a wide field of applications and these compounds can be easily disposed of with out enviermental risks[(12)] and several conductive blends of polyaniline with insulating polymers have been reported [(13,17)] Laska and others Prepared and investigated the following blends[(14)] Polyaniline /diisooctyl phosphate (DioHp)-PVC, Polyaniline/di(m-tolyl) phosphate (DPHP)-PVC.Polyaniline/diphenyl phosphate (DioHp)-PVC Polyaniline/diisooctylphosphate-poly (methylmethacrylate). Polyaniline/ diisooctyl phosphate-polystyrene.Polyaniline/diisooctyl phosphate-cellulose acetate-butyrate and Polyaniline/diisooctyl phosphate-cellulose properate. The most important domainat applications of conducting blends are in static materials conductivities of antistatic applications ,these blends must have electrical conductivity within the range (10^{-6} – 10^{-5}) $S.cm^{-1}$ [(18)]. V.Jousseame and others [(19)] investigated the influence of aging on electronic properties of polyaniline-polystyrine (PANI-PST) blend a remarkable notice.

In this article PANI-PVC blend was synthesized using condensation polymerization, while dilution of HCL (5%, 10% v/v) have been used as a dopant and many parameters corresponding to the homogenous film were identified. Also electrical conduction mechanism for the blend was analysed.

Experimental

PANI-PVC blend was synthesized by condensation copolymerization of PVC with aniline monomer were three necks reaction vessel of (500) ml volume charged with (0.1) mole aniline monomer purchased from Fulka Company the chemical formula ($C_6H_5NH_2$), Purum~99% (GC); B.P. 181-185° ;d 1.022; n 1.586., 1lt ≈ 1.02 kg and (0.1) mole PVC and (100) ml cyclohexanone .The reaction vessel provided by condenser, mechanical, stirrer and thermometer. The mixture was heated gradually up to (110)C by oil bath for 12 hours . The product was evaporated from the excess cyclohexanone after cooled to room temperature and then dried by rotary evaporator under vacuum pressure (0.1) mmHg at (30)C for 6 hours.

Aluminum substrate (2.5x2.5) cm^2 was thoroughly cleaned in acetone and washed with distilled water and dried at (100)°C for one hour in the air Polymer as thin film has been deposited on this substrate as a lower-electrode at normal equilibrium condition using cast method from solution technique, Then dried at room temperature for 24 hrs, after that heated gradually up to 50°C by a rate 10°C /30 mins, and then the cast films were kept at this temperature for 24 hrs to complete curing. Evaporation of Aluminum metal (99.99%) was carried out using evaporation system model (Varian 3117) under vacuum pressure more than (10^{-6} torr) as upper electrode.evaporationt takeplace through a circular mask 0.03cm^2 to obtain sandwich configuration.

A solution of HCL of 5% and 10 % concentration for performing electrical properties as a function of dipping time in 5% and 10% of HCL solution were Steady state current was measured with help of Keithley 417. The circuit of measurements was shown in fig (1). All (Current-Voltage) measurements were carried in a dark and electrical shield as a function of dipping time with dilution of HCL (5% v/v) and (10% v/v). All measurements have been made under darkness and temperature equal to 30)°C using electricall shield box.

Results & Discussion

In this study the variation of current or resistively as a function of dipping time in 5% , 10 % HCL solution was studied. The variation of current as a function of time is very important to detect the steady state condition which consider in some cases as a one of the major practical problems (especially in polymeric materials) due to the difficulties to obtain steady state current at a moderate cycle.

Fig(2) shows the relationship of current with time measured at room temperature after post curing at different field strengths for (PANI-PVC) blend this phenomenon may be related to the heat effect which activates the remaining traces of the solvent in the film and also effect of random motion of polymeric chains. Fig (3) shows the plot of current versus applied voltage for typical polymer films of 10μm thickness . The low field region (0-10) Volts were the thickness of measured films obtained by using mechanicl micrometer, the current shows Ohmic behavior which indicates the thermally generated charge carrier are effected by the current limits [9] .

The conductivity of the polymer films in the Ohmic region is shown in fig(4) where the conductivity is increase by increasing doping ratio with delusion of hydro chloride acid (5% v/v, 10% v/v) with maximum obtained electrical conductivity equal to $12.3x10^{-8}$ $S.cm^{-1}$ at dipping time 15 minutes with dilution of hydrochloride acid 5%, and for 10% the maximum conductivity reach to $5.2x10^{-8}$ $S.cm^{-1}$ at dipping time equal to 30 minutes as shown in fig (4), we can see that increasing dipping time has to fold effect ,first ,it may increase electrical conductivity due to the increase of charge carriers throughout breaking extra double bonds from the polymer backbone, second, it may decrease conjugation throughout smashing more bonds leading to an extra changes in polymer structure, such as, forming more defects and more trapping centers, and hence, leading to a small conjugation double bonds and wave function of charge carriers, similar to the results obtained by other researchers[18-19].

The conduction mechanism is obtained from plotting the (I-V) characteristic of the polymer. On LogI-LogV scale as shown in fig (5) at higher voltage ($V \geq$ 10 volts) shows anon-Ohmic region with the (slope≈2-3).The deviation from Ohmic law can be explained by space charge limited current from an insulation with shallow traps, where [13-14].

$$J=9/8[\mu_e \varepsilon_\circ \xi \Theta (V^2/d^3)]$$

$\varepsilon_\circ$ Is the permittivity of free space.

μ_e Is the electron mobility in conduction band.

This relation indicates that SCLC mechanism is a good suggestion to explain the charge transfer in this region and the extent to which traps reduce the effective mobility (μ_{eff}) of charge carriers and can be estimated from the relation[14-15]:-

$$\theta = P_o / (P_o + P_t) = I_1 / I_2.$$

Where I_1 is the current at critical voltage at which the transition to SCLC Conduction is occurring and I_2 is the current at the end of the rise.

θ is an important factor to know the changes that made to polymer backbone and structure specially to kind of effects such as deep and shallow traps this behaviour is shown Fig (6)which shows the relation between θ and dipping time, more details are obtained at dipping time equal to 15 mins. were localized state are less and there are enough compensation charge available since less localized state which can trap and store charge, and high conductivity while for 10% HCL best dipping time is 30 minutes.

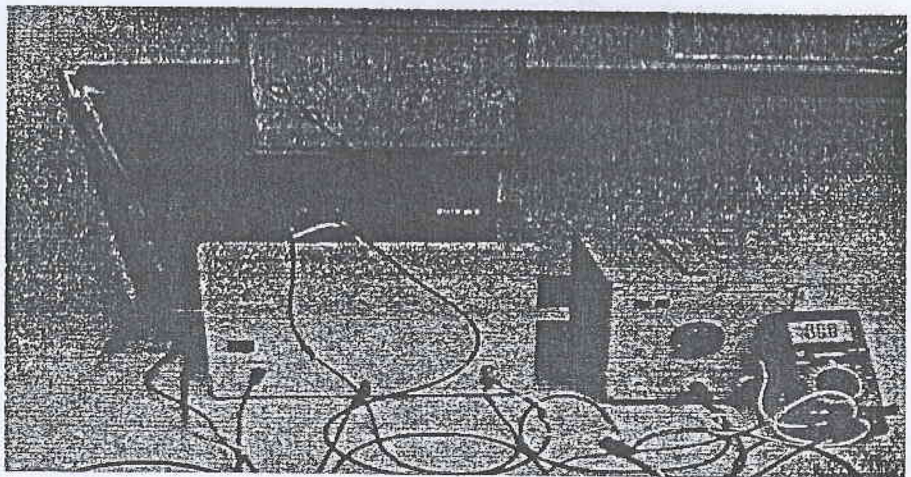


Fig (1); The circuit of (I-V) measurements.

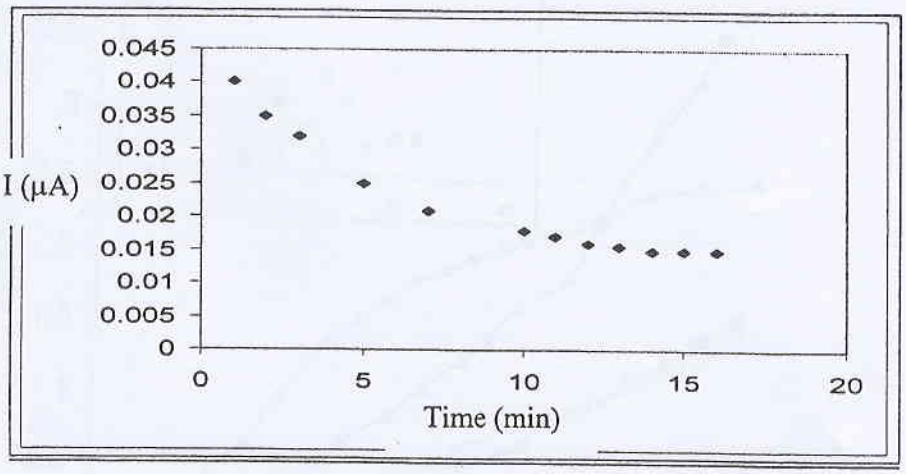
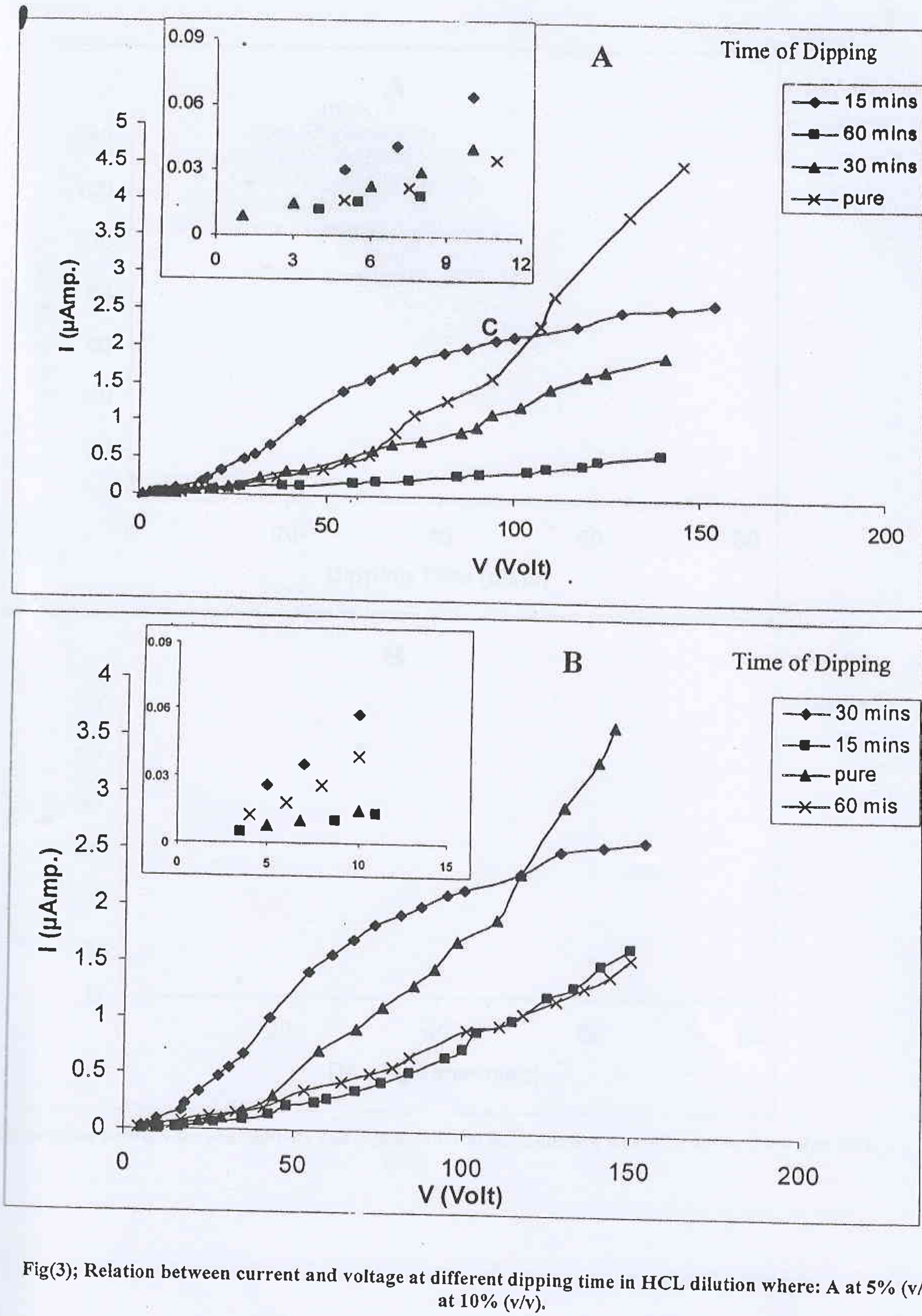
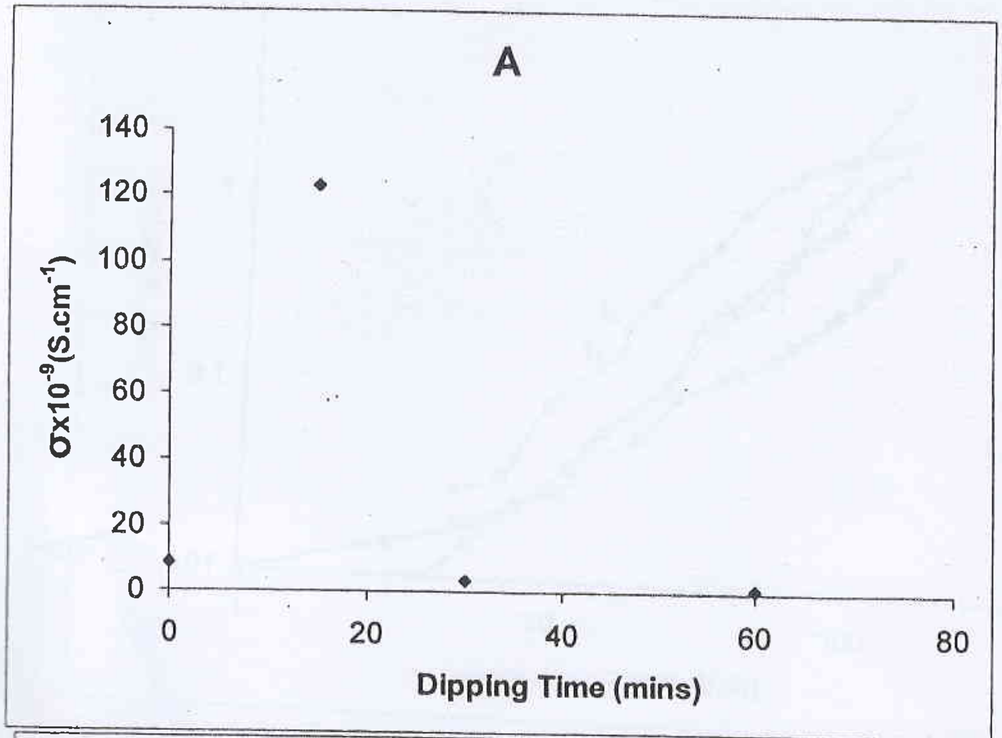
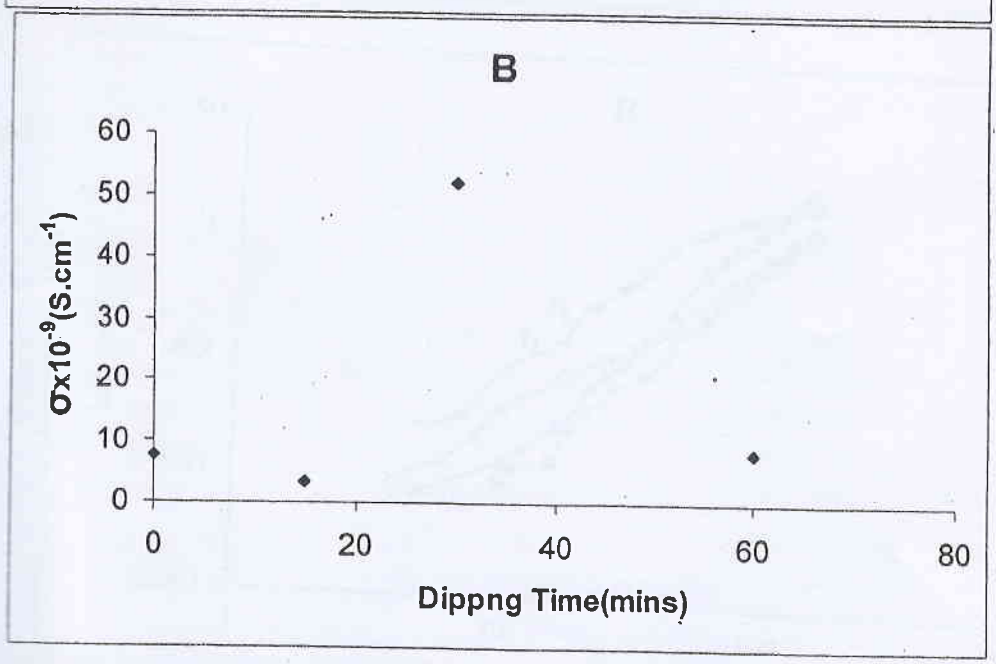


Fig (2); Variation of current as a function of time.

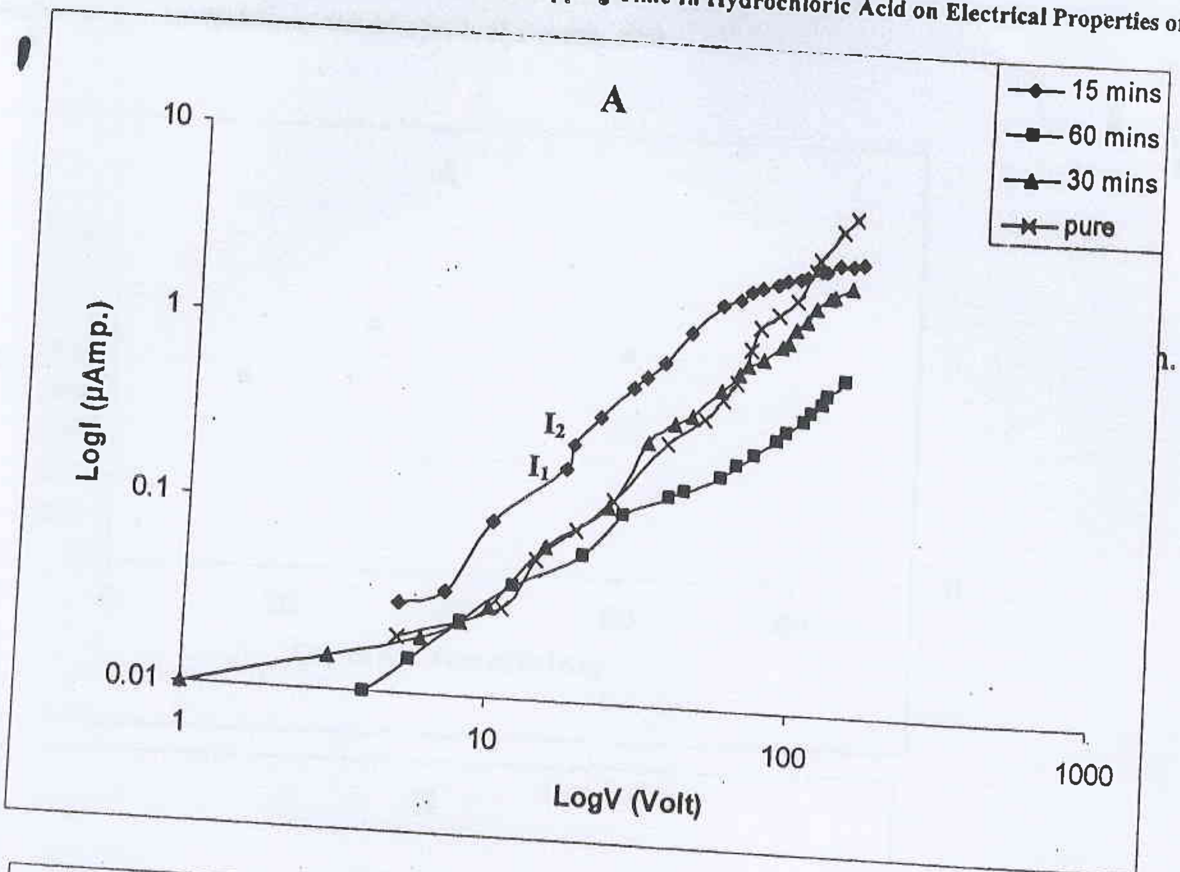


Fig(3); Relation between current and voltage at different dipping time in HCL dilution where: A at 5% (v/v), B at 10% (v/v).





Fig(4);The relation between the conductivity and dipping time in HCL dilution where: A at 5% (v/v), B at 10% (v/v).



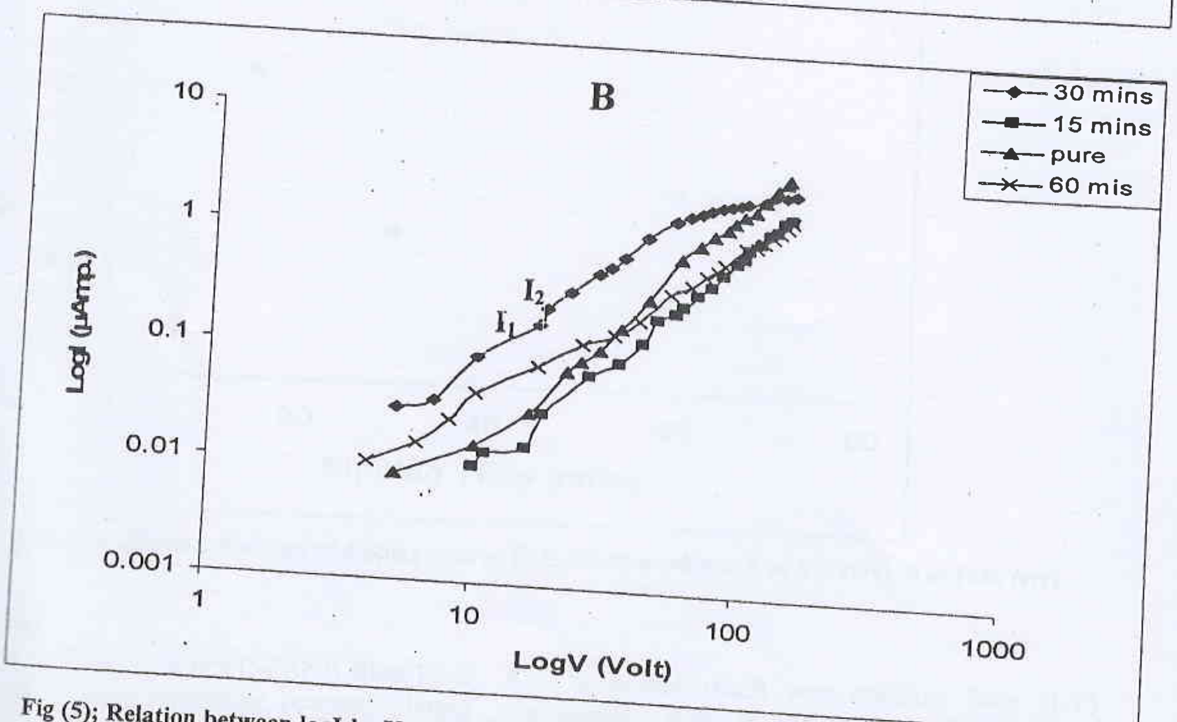


Fig (5); Relation between logI-logV as a function of dipping time in HCL dilution where: A at 5% (v/v), B at 10% (v/v).

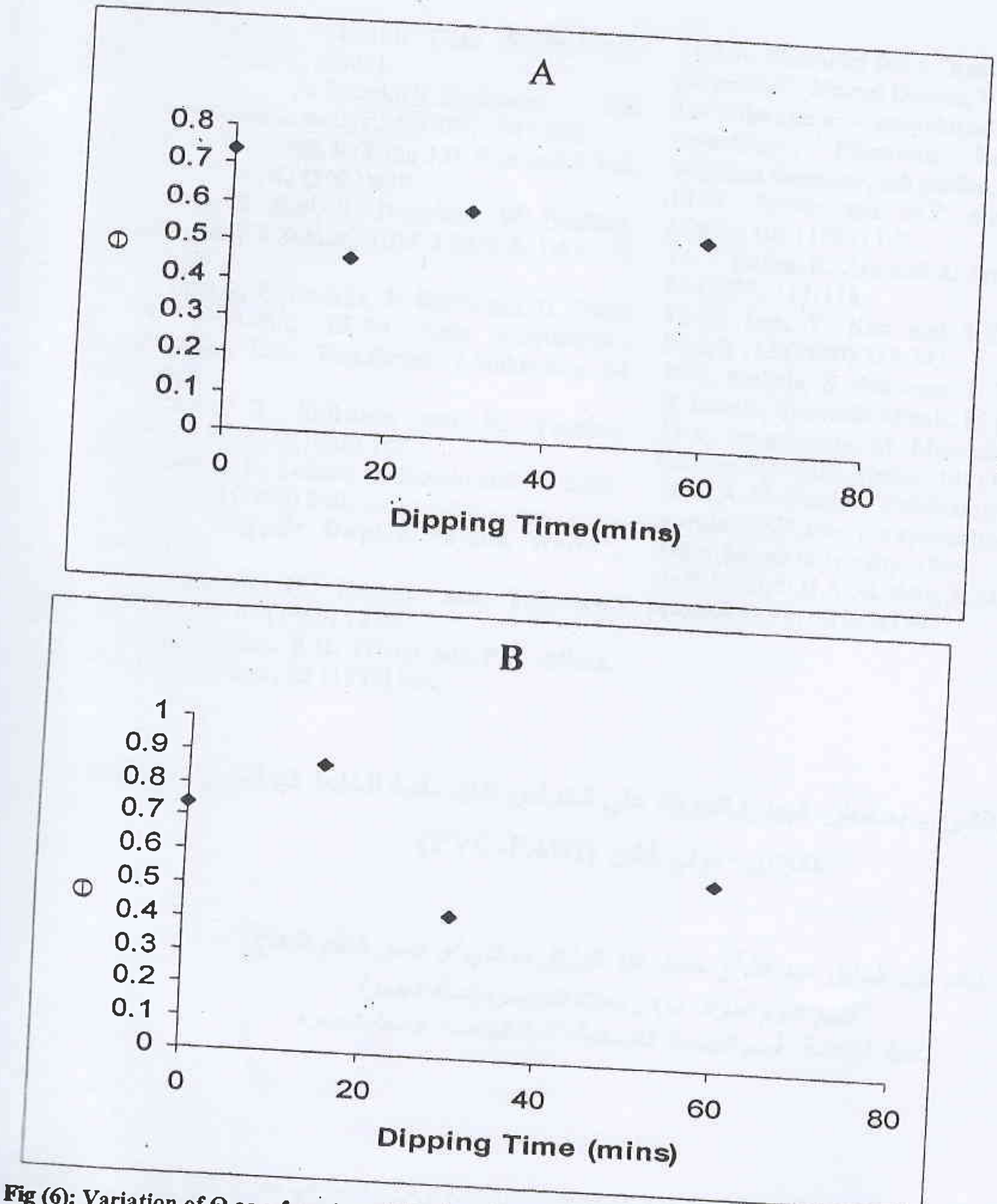


Fig (6); Variation of Θ as a function of dipping time in HCL dilution where: A at 5% (v/v), B at 10% (v/v).

Conclusion

Electrical properties of (PVC-PANI) films have been studied through measuring (current-voltage) characteristic as a function of doping with HCL (5%, 10%) (v/v) using the structure (metal/ polymer/metal). The obtained results show that the conduction mechanism was space charge limited current and highest conductivity was (12.3×10^{-8} $S.cm^{-1}$). Another result was obtained from (I-V) characteristic is the traps magnitude change due to doping ratio and minimum at doping ratio equal to (5% v/v) with 15 minutes dipping time. All the prepared polymeric films show semiconductor behavior.

References

1-G.P. Crawford **"Flexible flate display"**,John Wiely and Sons,NY, (2005).

2-S.Miyauchi ,Y.Kaneko,Y.Sorimachi and I.Tsubata, synthetic metals ,28(1989) c747-752.

3-S.S. Kim, Y.S. Choi, K. Kim, J.H. Kim and S. Lm, Appl.Phys. Lett., 82 (2003)639.

4-W. Riess, H. Riel, T. Beierlein, W. Brufting, P.Muller and P.F.Seidler, IBM J.RES & DEV, 45 (2001) 2001.

5-J. Paloheima, E. Punkka, P. Kuivalain, H. Stubb and P. Yli-Lahti, EL.64 Acta Polytechnica Sscandinavica, Elec. Eng.Scries, J.Sinkkohen, 64 (1989)178.

6-K. Kaneto, T. Shikaishi and K. Yoshino, Japn.J.Appl.Phys. 24(1985) 107.

7-J. Paloheimo, K. Laskso, H. Isotalo and H. Stubb, Synth.Met., 68 (1995) 249.

8-J. Kido, **"Organic Display Physics World"**, (1999) 27-30.

9- A. Tsumura, H. Keozuk and T. Anod, J.App.Phys.lett. 49 (1986) 1210.

10-J.H. Burroughes, R.H. Friend and P.C. Allens, J.Phys.D:Appl.Phys., 22 (1989) 956.

11-T.A. Shotheim (ed.), **"hand book of conductive polymers"** , Marcel Dekker, N.Y., (1988).

12-**"Ullmann's encyclopedia of industrial chemistry"**, Electronic Release, Wiky-CVH. Wenham Germany, 6th edition, (2002).

13-W. Jinwie and M.P. srinivasan , Synthetic Metals, 105 (1999) 1-7 .

14- J. Laska, K. Zak and A. Pron, Synthetic Metals, 84 (1997) 117-118.

15-W. Lee, Y. Kim and S.Y. Kanng, Synthetic Metals 113 (2000) 237-243.

16-T. Makela, S. Pienimaa, T. Take, S. Jussila and H. Isotalo, Synthetic Metals, 85 (1997) 1335.

17-V. Jousseaume, M. Mmorsli, A. Bonnet and S. Lefrant, Synthetic Metals, 101 (1999) 813-814

18- H.A.Al-ghanim, "Fabrication and study of poly pyrrole /n-Sillicon, it's application as FET, M.SC. thesis ,basrah university, 1998.

19-K.S.Majdi,H.A.AL.Attar,K,M,Zidan,Basrah research J.,Vol.0,No.0(1995).

دراسة تأثير زمن الشويب بحامض الهيدروكلوريك على الخواص الكهربائية للخليط البوليمري بولي كلوريد الفاينيل- بولي أنلين (PVC-PANI)

ناظم عبد الجليل عبد الله[1] و حميد عبد الرزاق حمادي[1] و عمار كاظم البعاج[2]

[1] قسم علوم المواد، مركز أبحاث البوليمر،جامعة البصرة

[2] كلية الهندسة، قسم الهندسة الكيميائية، كلية الهندسة' جامعة البصرة

المستخلص

في هذا البحث تم دراسة الخواص الكهربائية للبوليمر (PVC-PANI) كدالة لزمن الغطس في محلول مخفف بنسب (,10% 5%) من حامض الهيدروكلوريك (HCL) باستخدام التركيب (ألمنيوم-بوليمر-ألمنيوم) وباستخدام طريقة ثنائية القطب في القياس.تم قياس مميزة التيار- الفولتية في الحالة المستقرة، وأشارت النتائج المستحصلة إلى أن ميكانيكية التوصيل الغالبة للأغشية المحضرة هي التيار المحدد بشحنات الفراغ (SCLC)، وأن أقصى قيمة للتوصيلية الكهربائية هي ($12.3x10^{-8}$ S. m^{-1}) عند استخدام (5% HCL) و ($5.2x10^{-8}$ S.m^{-1}) عند (10% HCL) عند الأزمان (15 min) و (10 min) على التوالي.