

تَحْضِير تَرَائِب بُولِيمِرِيَّة وَدِرَاسَة بَعْض خِصَائِصِهَا لِلتَّوْصِيلَة الكهربائية, الميكانيكية والانتفاخية

الخلاصة:-

يمكن زيادة التوصيلية الكهربائية للبوليمرات بطرق عديدة ومنها إضافة الحشوات الموصلة إلى المادة البوليمرية العازلة . ومن أهم الحشوات الموصلة التي لاقت نجاحا تطبيقيا كبيرا في هذا المجال هي الحشوات الكربونية لكونها رخيصة الثمن وسهلة الاستخدام ويمكن الوصول إلى القيم المطلوبة من التوصيلية بنسب وزنية معينة .

شملت هذه الدراسة تحضير العديد من العينات البوليمرية الموصلة باستخدام تقنية القولية بالكبس وبطريقة (Sandwich) من خلال تحضير شرائح عديدة من البولي اثيلين الواطيء الكثافة (LDPE) وشرائح عديدة من البولي اثيلين العالي الكثافة (HDPE) ومزجها مع مسحوق البولي فنيل كلورايد (PVC) وداي-٢-اثيل هكسيل فتاليت (DOP) ومن خلال تفاعل التشابك , ثم إضافة مسحوق الحشوة (الكربون أو الكرافيت أو كلاهما) إلى الشريحة المحضرة ووضعها في قالب المكبس بسخان كهربائي .

درس في هذا البحث تأثير الحشوات الكربونية على المقاومة الكهربائية وثابت العزل الكهربائي لتركيبات محضرة من نوعين من البولي اثيلين الواطيء الكثافة (LDPE) والبولي اثيلين العالي الكثافة (HDPE) . وجد إن تركيبات البولي اثيلين عموما المحشوة بأسود الكربون تمتلك مقاومة كهربائية اقل (أي تمتلك توصيلية كهربائية أعلى) من تلك المحشوة بالكرافيت .

درس في هذا البحث تأثير مزج حشوة اسود الكربون مع حشوة الكرافيت بنسب وزنية مختلفة على المقاومة الكهربائية وعلى ثابت العزل الكهربائي كدالة للزمن ودرجة الحرارة , فوجد إن هناك نسب مزج مثلى تعطي تركيبات اقل مقاومة كهربائية (أعلى توصيلية كهربائية) من بين نسب المزج كم في الجداول من (١٣-٢ - ٨ - ٢) , وكذلك تم حساب طاقات تنشيط

التكوين للتركيبات البوليمرية المحضرة كما في الجدول (٣-١) من خلال رسم الميل بين لوغاريتم ثابت التوصيل الكهربائي ومقلوب درجة الحرارة المطلقة ($\log k$ مقابل $1/T$) من خلال المعادلة :

$$\text{Log } K = \log K_0 - [\Delta U / 2.303 RT]$$

ووجد ان قيم طاقة التنشيط لكل السبائك البوليمرية المحضرة عالية نسبيا , وان طاقة التنشيط العالية تمثل زيادة في الثباتية الحرارية للبوليمر.

أن الجزء الثاني من الدراسة تضمن دراسة الخواص الميكانيكية مثل تعيين ودراسة كل من :-

١- منحنيات الإجهاد التوتر Stress – Strain

٢- قوة الصدم Impact Strength

٣- الصلادة Hardness

وتم حساب العديد من المعاملات المعبرة عن الخواص الميكانيكية مثل قوة الشد (σ) والاستطالة (%E) وغيرها .

دلت نتائج الفحوصات للتراكيب البوليمرية المحضرة في المحور السابق إلى زيادة في قيم قوة الشد والصلادة مع زيادة نسب الحشوات (اسود الكربون و الكرافيت) إلى السبيكة مقرونة بانخفاض نسبة الاستطالة وقوة الصدم , واستدل من هذه الدراسة إمكانية السيطرة على الخواص الميكانيكية وإبراز المهمة منها حسب استخداماتها الصناعية .

تم قياس الخصائص الميكانيكية لتراكيب بوليمرية محضرة أخرى باستخدام تقنية القولية بالكبس وبطريقة (Sandwich) من مزج البولي اثلين الواطيء الكثافة (LDPE) مع نسب مختلفة من البولي اكريل امايد (PAM) وباستخدام عوامل تشابك مختلفة وبنسب مختلفة

(هكسامثيلين تترامين HM و الكلوترالياهويد Ga وثلاثي بيوتيل بيروكسي-2-اثيل هكسانويت C₁₇) , دلت النتائج على زيادة قوة الشد للبوليمرات المحضرة مع عاملي التشابك (Ga , C₁₇) ونقصان قوة الشد مع عامل التشابك (HM) , ونقصان في قوة الصدم والمرونة للبوليمرات مع عوامل التشابك الثلاثة .

ودلت نتائج الصلادة (Shore A) تزداد عند نسبة (PAM ٢.٥% wt.) بوجود عامل التشابك (HM) وتزداد عند نسبة (PAM ٢% wt.) بوجود عامل التشابك (C₁₇) وتزداد عند نسبة (PAM ٤% wt.) بوجود عامل التشابك (Ga) .

ودلت نتائج الصلادة (Shore D) تزداد عند نسبة (PAM ٢.٥% wt.) بوجود عامل التشابك (HM) وتزداد عند نسبة (PAM ١,٢% wt.) بوجود عامل التشابك (C₁₇) وتزداد عند نسب (PAM ١,٢%wt.) بوجود عامل التشابك (Ga) .

وتم تشخيص البوليمرات المحضرة في هذه الدراسة بتقنية الأشعة تحت الحمراء (FT.IR)

وخصص المحور الثالث من الدراسة على تحضير تراكيب بوليمرية هلامية من البولي اثلين الواطء الكثافة (LDPE) مع البولي اليكترولايت (PE) المستخدم في أحواض التركيد لإنتاج الماء من نوع (R . O) ونسب مختلفة لغرض الحصول على تراكيب هلامية لها القابلية على خزن أعلى كمية من الماء داخلها وذلك باستخدام عدة عوامل تشابك مثل (هكسامثيلين تترامين HM و الكلوترالياهويد Ga وثلاثي بيوتيل بيروكسي-2-اثيل هكسانويت C₁₇) وبنسبة (٥%wt)

وتم دراسة عملية امتصاص الماء (نسبة الانتفاخ (Q)) من قبل التراكيب البوليمرية وعملية فقدها للماء كدالة للزمن .

أظهرت النتائج إن التراكيب البوليمرية الهلامية لها قابلية عالية على الاحتفاظ بالماء لفترات زمنية أكثر من (٤٨ ساعة) ,وتزداد نسب الانتفاخ (Q) بزيادة نسب (PE) .

ووجد بان نسب الانتفاخ (Q) تزداد وكذلك زمن فقد الماء للتراكيب الهلامية باستخدام عوامل التشابك وحسب تسلسلها (HM < C_{٦٧} < Ga) .

وتم تشخيص التراكيب البوليمرية الهلامية المحضرة في هذه الدراسة بتقنية الأشعة تحت الحمراء (FT.IR) .

Preparation of Polymeric Composites and study of some Electrical Conductivity , Mechanical and Swelling Properties

Abstract :-

The electrical conductivity of Polymers can be increased by many methods such as the addition of conductor filler to the insulator polymer . Carbon filler was one of the most successful conductor filler used due to its ease of use as well as low cost .

In this study , many polymeric conductors were prepared using molding press technique and sandwich method by preparing sheets of low density polyethylene [LDPE] and sheets of high density polyethylene [HDPE] and mixed with powder of polyvinylchloride [PVC] and di- γ -ethylhexyl phthalate [DOP] . Then filler powders (carbon or graphite or both) were added to the prepared sheet and place in molding press in electric oven .

The first part in this study includes the effect of carbon filler on electrical resistance and dielectric constant for the above prepared polymers were studied . It was found that polymers filled with carbon black has less electrical resistance (high electrical conductivity) to those filled with graphite . The effect of mixing carbon black filler with graphite filler at different weight ratio on the electrical resistance and dielectric constant as a function of time and temperature were also studied . An

optimum mixing ratio which gives low electrical resistance. Also the combination activation energy of the prepared polymers was calculated using vant Hoff plotting . It was found that the combination activation energy was high for all prepared polymeric alloys which indicate an increase in the thermal stability of the polymers .

The second part of this study includes studying the mechanical properties i.e. determination and study of :

1- Stress – Strain Curve .

2- Impact Strength .

3- Hardness .

The prepared polymers were identified using (F.T.I.R) .

Many factors related to mechanical properties such as Tensile Strength [σ] and Elongation [%E] were calculated .

The investigation results of the prepared polymers showed an increase in tensile strength values with increase of filler (carbon black and graphite) to an alloy ratio accompanied with depression of elongation ratio as well as impact strength .

It is concluded from this study that it's possible to control the mechanical properties according to its industrial uses .

The mechanical properties of another polymers prepared by mixing [LDPE] with different ratio of Polyacrylamide [PAM] using different ratio of different cross linking agents [HM , Ga and C_{1v}] were carried out .

The result showed an increase in tensile strength of polymers prepared with the cross linking agents [Ga and C_{1v}] . While a decrease in tensile strength was noticed with cross linking agent [HM] . An decrease in impact strength and flexibility of polymers were noticed using the three cross linking agents [HM , Ga and C_{1v}]

The hardness results (shore A) showed an increase at weight ratio (2.0 % PAM) in the presence of [HM] as cross linking agent. While it is increased at weight ratio (2% PAM) in the presence of (C_{1v}) as cross linking agent and increased at weight ratio of (2% PAM) in the presence of (Ga) as cross linking agent .

The hardness result (shore D) showed an increase at weight ratio (2.0% PAM) using (HM) as cross linking agent and increased at (1,2% PAM) using (C_{1v}) as cross linking agent and increased at (1,2% PAM) using (Ga) as cross linking agent .

The third part of this study concerns on the preparation of gel polymers from [LDPE] used to produce (R.O) water at different ratios in order to obtain gel structure capable of storage high quantity of water

through the use of different cross linking agent such as [HM , Ga and C_{1v}] at ratios of (% wt.) .

The prepared gel polymers were identified using (F.T.I.R) .

Water absorption process (Swelling ratio Q) and the process of water loss as a function of time were also studied .

The result showed that gel polymers has high ability to store water for period more than (ϵ^{\wedge} hrs.) . The Swelling ratio (Q) increased with the increasing in the percentage of [PE] . It was also found that Swelling ratio (Q) increased as well as an increase the time of water loss for gel structure using cross linking agent in the order

$$\text{Ga} > \text{C}_{1v} > \text{HM}$$

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**Preparation of Polymeric Composites
and study of some Electrical
Conductivity , Mechanical and Swelling
Properties**

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مؤخر نراكيب بوليمرية دورانية بعض خصائصها للتوصيلة

والكهربائية، والميكانيكية والأدفاخية من

عامر موسى جودة ألدشمري

رسالة مقدمة إلى كلية العلوم

جامعة بابل

كجزء من متطلبات نيل درجة الدكتوراه في فلسفة

الكيمياء – الكيمياء الفيزيائية للبوليمرات

بأشراف

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مايس ٢٠٠٦

ربيع الثاني ١٤٢٧

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

الرَّحْمَنُ * عَلَّمَ الْقُرْآنَ
* خَلَقَ الْإِنْسَانَ * عَلَّمَهُ
* الْبَيَانَ *

صدق الله العلي العظيم

الرحمن / الآيات (١ - ٤)

Dedication

To

My Father Spirit

My Wife

My Daughters

Malak & Retag

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Abbreviations

IPN's	Inter penetrating polymer network
LDPE	Low density polyethylene
HDPE	High density Polyethylene
LLDPE	Linear low density polyethylene
PVC	Polyvinyl Chloride
DOP	Di- γ -ethylhexylphthalate
C	Carbon Black
G	Graphite
PAM	Poly acrylamide
HM	Hexamethylene tetramine
C _{7v}	t-Butyl peroxy γ -ethylhexanoate
PE	Polyelectrolyte
Ga	Gluteraldehyde
PDC	PVC +DOP +C
PDG	PVC +DOP +G
PDCG	PVC +DOP +C +G

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Interoduction

1-1 - *Mechanical Properties of Polymers*

The mechanical properties are the most important properties among all properties of Polymeric materials, since all condition, The majority of end – Use applications involve some degree of mechanical loading. Never the less, the material selection for a variety of application is quite often based on their mechanical and thermomechanical properties, Such as tensile, modulus, elongation, hardness, and impact strength⁽¹⁻³⁾.

Its important to a cqaint to the technical terms and concepts used to describe the polymers properties. Since these standarised terms are used by suppliers and users to communicate how the material behavior under specific conditions.

1- 1- 1 : **Stress – Strain Curve**

The stress – strain test is the most widely used of all mechanical tests, the polymeric materials can be broadly classified in terms of their relative softness, brittleness, hardness, and toughness. The tensile Stress – Strain diagrams serve as a base for such classification, the area under the Stress – strain curve represents the toughness of the polymeric material⁽³⁾.

Fig. (1-1) illustrates typical stress – strain Curves for several type of polymeric materials.

- 1- Soft and weak material Characterized by low modulus, low yield stress and moderate elongation at break point, poly tetrafluoroethylene (PTFE) is a good example for such type of polymeric material.
- 2- Soft but tough materials show low modulus, low yield stress but very high elongation and high Stress at break, poly ethylene is classic example for this type of polymers.
- 3- Hard and brittle material is characterized by high modulus, and low elongation, it may or may not yield before break, an example for this type of polymers is phenolic resins.
- 4- Hard and strong material has high modulus, high yield stress usually high ultimate strength, and low elongation Polyacetel is a good example of this Class of materials.
- 5- Hard and tough material is characterized by high modulus, high yield stress, high elongation at break, Polycarbonate is considered as hard and tough material.

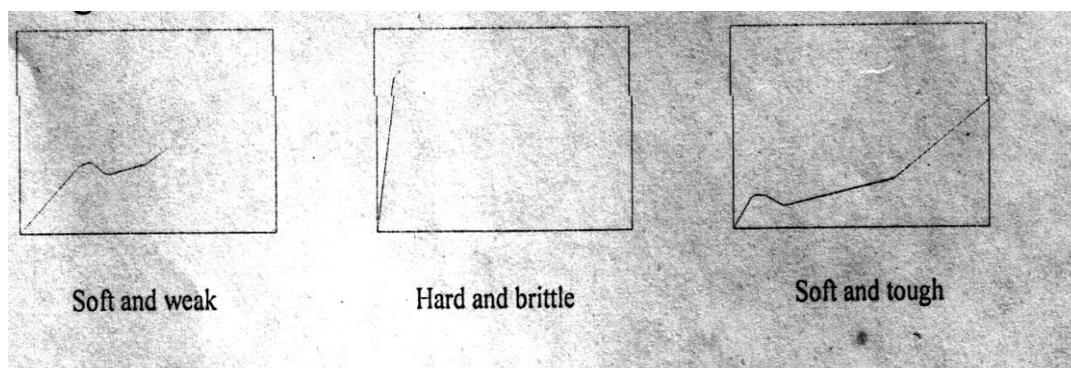


Fig. (1-1) Typical stress – strain curves of different types of polymeric materials

The generalized mechanical properties of various polymeric classes are summarized hown in Fig. (1-2) .

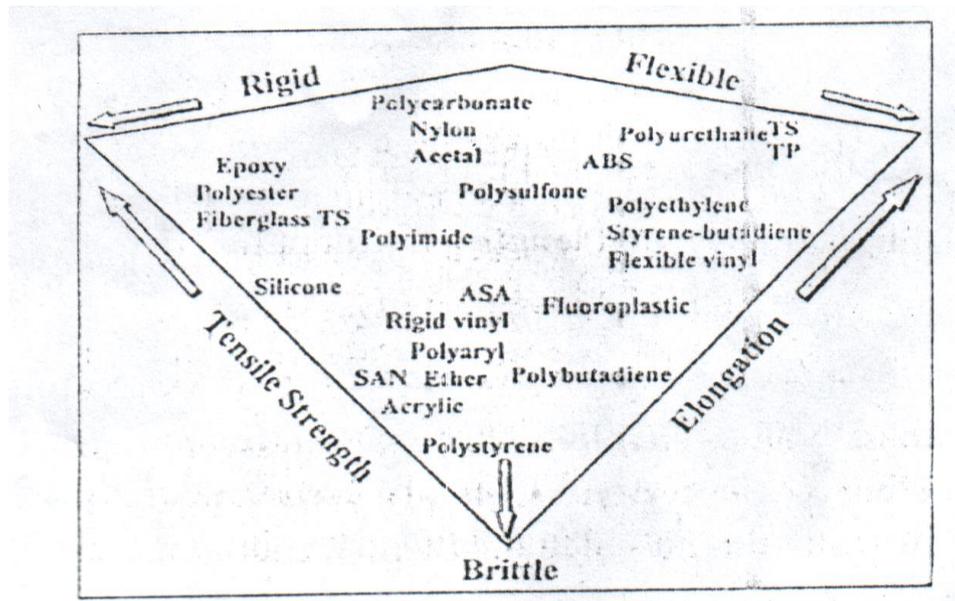


Fig. (1-2) Mechanical properties of various polymeric classes

Fig. (1-3) illustrate the terminology used for stress – strain testing slope of the initial straight line portion of the curve represent the elastic modulus of material which is represent by :

$$E = \frac{\text{Stress}}{\text{Strain}} = \frac{\Delta\sigma}{\Delta\epsilon} \quad \dots\dots\dots(1-1)$$

The maximum in the curve denotes the tensile strenght at yield (σ_y) and elongation at yield (ϵ_y) , (the yield point is that point when the material is subjected to load tensile , compressive etc. and will no longer return to its original or shape when the load is removed) .

The end of the denotes the fracture of material , which is characterized by the tensile strength at break (σ_B) and the ultimate strain or elongation at break(ϵ_B)⁽⁴⁾ .

These mechanical properties can be evaluated by the following experimental relationships which are usually expressed in (Kg. F/cm²)^(°).

$$\text{Tensile strength } (\sigma) = \frac{\text{Force load recorded (F)}}{\text{Area cross section of the sample (A)}} \dots\dots\dots (1-2)$$

$$\text{Tensile strength at break } (\sigma_B) = \frac{\text{Load recorded at break}}{\text{Original area cross – section of the sample(A)}} \dots (1-3)$$

$$\text{Tensile strength } (\sigma_y) = \frac{\text{Maximum load recorded (F)}}{\text{Area cross section of the sample (A)}} \dots\dots\dots (1-4)$$

$$\text{Strain} = \frac{\text{Final length} - \text{original length}}{\text{original length}} = \frac{\Delta L}{L} \dots\dots\dots (1-5)$$

The modulus values should not be determined from the results of one stress – strain curve , several tests should be made on the material and the average modulus where calculated which indicate the standard deviation .

The molecular orientation has a significant effect on tensile strength values .Therefore these values should be indicated by the direction of orientation . On the other hand the stress – strain parameters are extremely temperature dependent⁽¹⁾ . In addition these parameters are thermal treatment dependence^(°-Y) .

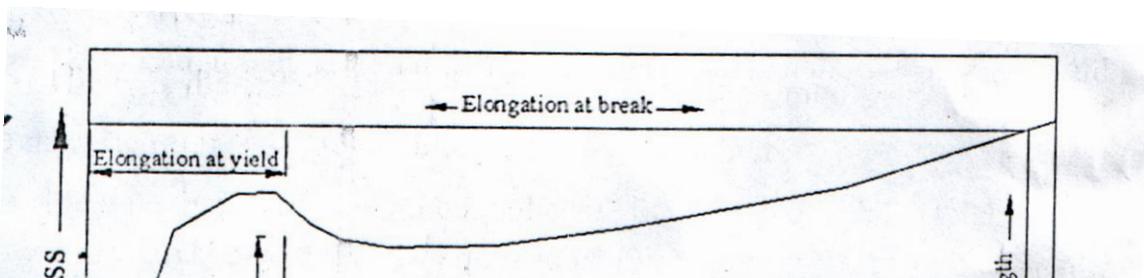


Fig. (1-3) Typical, generalized tensile stress – strain curve for polymers

1-1-2 - **Impact Strength Tests**

The impact properties of the polymeric materials are directly related to the overall toughness of the material (toughness is the ability of polymer to absorb applied energy).

The impact strength is a measure of toughness. Therefore the higher the impact strength of material the higher the toughness and vice versa. While the impact resistance is the ability of the material to resist breaking under a shock load or its ability to resist the fracture under stress applied at high

rate (1-4).

There are several impact tests to measure the energy required to break the standard samples under certain specified conditions. The most widely used tests are the Izod and Charpy impact test which are both (Pendulum type) instrument with notched samples. When the samples are struck on the free end is known as Charpy impact test while when the samples are supported at the two ends and struck on the face opposite to the notch of the specimen, the test is known as Izod impact test (1-5).

The reason for notching the specimen is to provide a stress concentration area that promotes a brittle rather than ductile failure.

A notch in test specimen or a sharp corner in fabricated part drastically lowers the impact strength. Both notch depth and radius remarkable effect on the impact strength of the materials. The impact strength of polymer material is strongly dependent upon temperature, because more mobility of the chain polymers at higher temperature test, the impact strength significantly increased (1-6).

The impact strength of thermosetting varies slightly with temperature over a wide range. Crystalline polymers have high impact strength, increasing the percentage of crystallinity [glass transition (T_g) well below the test temperature] will reduce the impact strength and increase the probability of brittle failure. Reduction of the average molecular weight tends to reduce the impact strength and vice versa (1-7).

The impact strength can be calculated using the following relationship :

$$\text{Impact strength (KJ/m}^2\text{)} = \frac{\text{Fracture energy}}{\text{Area under the notch}} \dots\dots (1-6)$$

The Izod impact strength of number of common polymer at room tempure are listed in table (1-1) .

Table (1-1) Standard data for impact and hardness for several important commercial polymers .

Polymer	Izod impact strength ASTM D2760 (KJ/m ²)	Shore D hardness
Polyethylene(LDPE)	>0.0	09
Polyethylene (HDPE)	1.0	71
Polystyrene	6	78
Phenol-formaldehyde resin	1.0	82
Melamine formaldehyde resin	1.0	90
Unsaturated polyester resin	1.0	82

1-1-3 - **Hardness Test**

The hardness of polymeric materials is defined as the resistance to local deformation which is a complex property related to some mechanical properties of materials, i.e. modulus and strength (°).

The relationship to mechanical properties usually is a tendency for high modulus and strength, and their correlation with higher degrees of hardness for different classes of materials.

Therefore hardness has no simple definition, it can be measured and expressed only by carefully standardized techniques (°).

The hardness of all plastic materials decreases with temperature increase, on the other hand the surface finishing has a significant effect on hardness test result, a smooth molded surface yield higher value than machined surface, also the hardness value may depend upon the type and amount of fillers present in the sample and the degree of crosslinking (°).

Gouza classifies hardness tests into three types (°).

- 1- Hardness tests that measure the resistance of material to indentation by an indenter, examples Brinell hardness, Vickers hardness and shore durometers.
- 2- Hardness test that measure the resistance of material to scratching by another materials or by a sharp point. Example are Bierbaum hardness and Moh hardness.
- 3- Hardness tests which measure rebound efficiency or resilience. Example is Reckweel hardness.

The Duremeter hardness test is the most widely used for measuring the relative hardness of soft material, the test method is based on the penetration of specified indenter force into the material.

Two types of Durometers are most commonly used, type (A) and type (D). The basic difference between the two types is the shape and dimension of the indenter. Type (A) Durometer is used with relatively soft material, while type (D) Durometer is used with slightly harder materials. The hardness data for some Common polymer at the room temperature are listed in Table (1-1).

1-1-4 - **Fracture Energy**

The fracture process usually occurs in three stages the initiation of cracks, its stable growth under rising or constant load and its unstable propagation. These stages which necessary occur in all

materials ; a brittle which contains inherent flaws , such as weak grain boundaries in some brittle plastics and ductile materials . Unstable fracture precedes by the initiation and growth of the cracks which occur Via crazing mechanism in plastic , while crack initiates unstable propagation take place through the plastic region which are intrinsically capable of absorbing a great deal of energy during fracture .The area under stress – strain curve measure the fracture energy of the tested material .

Several factors affect the fracture energy of polymeric material some of them are structural factors which depend on the chemical structure and the composite constituents .

Other factors are external factors (environmental) factors e.g. thermal treatment , annealing , percent of crystallinity , presence of solvents (Solvent stress cracking) etc. Accordingly all factors should be taken into consideration when studying the fracture energy and the evaluation of this important parameter (K_{Ic}) .

1- 2- **Electrical Conductivity of Materials**

1- 2- 1 - **General Introduction**

polymers are generally good electrical insulators because they contain very low concentration and low mobility of free charge carriers . Many efforts were carried out to prepare conductive polymers and using them in various application due to their excellent physical and chemical properties.

These efforts can be Categorized into the following main areas :

- 1- Conjugated conductive polymers (intrinsically Conductive) $(1^{\circ} - 2^{\circ})$.
- 2- Ionic polymers (Poly electrolytes) $(2^{\circ}, 2^{\circ})$.

- ζ- Polymeric Tetracyanoquinodimethane (TCNQ) (27) .
- η- Polymers containing conductive fillers (28) .
- θ- Non – Conjugated conductive polymers (29, 30) .
- ι- Organometallic polymers (27, 31-33) .

The embedding of conductive fillers in an insulating polymer matrix is one of the widely – used methods to achieve conductive polymeric Composites . can be easily processed and shaped into various complicated aspects .

Composites are , generally , multiphase materials whose components are mechanically separable and exhibit properties unattainable in any of the Constituent phases (34) .

Various types of highly conductive fillers are used to produce polymer Conductive composites including metal powders or fibers (35-39) , metal Chlorides (40, 41) , conductive ceramics (42-44) , conjugated polymers (45-50) , Carbon and graphite (51-53) and Carbon nanotubes (54-56) .

Many problems correspond to the intrinsically Conductive polymers , such as: weak mechanical properties , unstable conductivity level , environmental instability , insolubility in organic solvents , intractability and many other problems which prevent the use of these materials in several industrial applications(27) .

Due to the above problems the scientific and Commercial interests direct towards the electrical conductive polymer composites . these materials provide unique electrical and mechanical properties as well as many excellent properties of polymeric materials , such as light weight , low cost , ease of processing and corrosion resistance compared with metals (18) .

The art of making a good conducting composite is to use the minimum quantity of conductive fillers to achieve the required degree of electrical conductivity (σ) . So , the Composites based on metal powders usually correspond to high filler concentration , for example (80% w/w) for nickel powder to achieve $\sigma = 1.5 \times 10^{-1}$ (S/cm) and (80% w/w) for silver powder to achieve $\sigma = 1.5 \times 10^4$ (S/cm) (69) . This high concentration tends to destroy the desirable mechanical properties of the plastic , that left the composite to be stiff , brittle and cannot be tailored .

Carbon black and graphite are widely used to produce conducting plastics because they are compatible materials, mixing in, adhering well to the polymer matrix, do not change the overall density very much and they are cheap. Recently Carbon nanotubes were used to achieve good conducting composites with only 1% w/w filler content.

The possible applications of electrically conductive plastics include electromagnetic frequency interference (EMI) shielding for electronic devices. The moderately conductive composites are used for processing parts such as fuel gauges and electrostatic dissipation (ESD), conducting coating, sensors and many other applications.

The major use of conductive rubber and plastics is to dissipate static charge. The most important uses of antistatic materials are those associated with hospital operating room, the petroleum industry and industries which produce powders or explosive substances. In these locations the danger of spark formation due to static charges and subsequently, of fire or explosion, exists. Therefore conductive rubbers and plastics are needed for production of variety of items used in various applications.

1-2-2- Electrical Conductivity

When a potential difference ($\Delta\Phi$) is applied across any material, an electric field (E) developed within the solid. If the field is uniform, ($E = \Delta\Phi / l$) where (l) is the length of the sample. Once the field developed, there is always a flow of current (I) through the materials. If (A) represent the cross-sectional area of the sample, the electrical conductivity σ can be defined as

$$\sigma = I l / A (\Delta\Phi) \dots\dots\dots (1-7)$$

For a uniform field,

$$\sigma = J / E \dots\dots\dots (1-8)$$

Where J is the current per unit area, usually called the current density.

Electrical conductivity and current resulted directly from the flow of charged particle. In general, an electric field accelerates a charged particle and causes it to attain a velocity (V). If there

is a concentration of (n) particles per unit volume of charge (q) moving with an average velocity (V), the current density is given by :

$$J = n q V \dots\dots\dots (1-9)$$

Where (q) measured in coulombs . The microscopic contribution to the electrical conductivity is obtained by combining Eq . (1-8) and (1-9) to yield :

$$\sigma = n q \mu \dots\dots\dots (1-10)$$

Where $\mu = V / E \dots\dots\dots (1-11)$

the velocity per unit field and μ is called the mobility .

It is to be noted that electrical transport by its nature , is a nonequilibrium process . An external electric field must be applied in order to obtain a current . This external field is a force that destroys thermodynamic equilibrium . It induces flow of charged particles , which can be accurately measured once a steady state is achieved .While no current flow in the absence of applied field. Thus , the electrical conductivity can be defined as the limit of the quantity in Eq . (1-8) for arbitrarily small fields :

$$\sigma = \lim_{E \rightarrow 0} (J/E) = (\partial J / \partial E)_{E=0} \dots\dots\dots (1-12)$$

With this definition , (σ) is independent of field . The low – field region is then the region in which the linear relation in equation (1-12)

$$J = \sigma E \dots\dots\dots (1-13)$$

Is obeyed . Equation (1-13) is known as ohm's law , and it is valid for most semiconductors .

1-2-3- **Classical Theory of Electrical Conductivity**

The classical theory of electrical conductivity was suggested by Thompson and Drude formulated a theory of metallic conduction by applying the methods of the kinetic theory of gases to outer electrons in a solid . Drude assumed that the outer electrons were easily separated from their ion cores . The much more massive ion cores were then taken as fundamentally fixed , while the detached electrons were assumed to be able to move freely throughout the solid (18, 19).

A justification of this assumption follows from the fact that thermal velocity (i.e. , the velocity attained solid at its ambient temperature) is almost three orders of magnitude larger for electrons than for ion cores . Drude further assumed that the outer electrons move freely without interactions with either the ion cores or the other electrons for an average time T , known as the relaxation time . After this time , collisions with either other electrons or the ion cores tend to restore thermodynamic equilibrium . Evidently , something is seriously wrong with the Drude model (100) . The answer to this problem did not emerge for more than 20 years , because it required the development of quantum mechanics .

1-2-4- **Quantum Theory of Electrical Conductivity**

The most important modification of classical theory is so far as electronic transport is concerned in the Pauli exclusion principle , the prohibition of more than one electron from simultaneously occupying the same energy level . This principle qualitatively changes the nature of both the ground state and the current –carrying states of all solids . The solution of quantum – mechanical problem begins with the calculation of the density of electronic energy levels , $g(\epsilon)$, as a function of their energy E . The major results for cases of solids as follows (18) :

- 1- The levels available to any electron as it moves through the crystal has energies that lie only in certain ranges , which are called energy bands . Regions of forbidden energies , called gaps that separate these bands .

- ϒ- For a periodic crystal , all the electronic states are decolorized , that is , every electron has the same probability of being found in the vicinity of any equivalent atom in the crystal . This result has never been demonstrated for the case of amorphous solids .
- ϓ- An electron in level near the botom of a band contributes positively towards the electronic conductivity ; in the presence of a pplied field , its a ccelerated toward the more positive potential and it rises in the band as it picks up energy from the field .
- ξ- In a crystal , the electron is scattered only deviation from periodicity , i.e. , defects impurities .

1- ϒ-σ - **Electrical Conductivity of Metals**

The electron theory of solids aims to give a satisfactory account of electrical conduction in metals , and to explain the existence of metallic , semi conducting and insulating behavior in different types of solids .

Electrical conduction involves the acceleration of the electron and distributed until a steady state is reached , when the momentum being gained from the fild balance that being lost to the lattice by sacttering processes . This is reached in avery short time t . In an idealized model , the conductivity σ is given by :

$$\sigma = ne^{\gamma} t / m \dots\dots\dots (1-16)$$

Where e , n and m is the charge , number and mass of the conduction electron respectively. It is often convenient to talk in tems of mean free path or inter – collision distance ℓ of the electrons , which will be approximately equal to t times the electrons velocity . The most important developments in the basic theory were the recognition that :

- 1- Since the electrons energy states are distributed over a few electron volts , the a ppropriate velocity of electrons that can change their states is nearly temperature – independent ($\sim 1.0^7 \text{ ms}^{-1}$).
- ϒ- A quantum – mechanically permitted state of an electron in a perfect crystal is one of infinite ℓ . As a result , the conductivity of a metallic material can be discussed in terms of the effective number of free electrons , and the factors that limit the mean free path .

1- 2- 7- **Electrical Conductivity Properties**

The major characteristic of insulator is their enormous electrical resistance, typically a factor of (10^{10} ohm) larger than in good metals ⁽¹⁹⁾. The extreme sensitivity of modern electrometer enables the detection of ultra small currents without any difficulty, so that the electrical conductivity of insulators can be measured with extreme accuracy.

The various mechanics for direct current (DC) flow in such materials turn out to be of great theoretical interest. In addition, the AC conductivity and photoconductivity of insulators have been exploited commercially in electronic devices such as electrophotographic copying machines.

Finally breakdown effects are of the almost importance in determining the dielectric strength of insulators in their major function as the means for electrical insulation.

1- 2- 7- 1- **Band Conduction**

The energy levels available to any electron in a solid is called bands, which are separated by regions of forbidden energies, called gaps.

Insulators are those solids in which there are a sufficient number of electrons to just fill all of the lowest – energy bands while leaving all higher – energy bands empty. If there is a relatively large ($> 3.0 \text{ e.v}$) gap between the highest filled band, known as the valence band, and the lowest empty band, known as the conduction band, then the material is an insulator ⁽¹¹⁶⁾. Since thermal energy at room temperature is only about (0.025 e.v) , there are very few free carriers in an insulator under equilibrium conditions. Nevertheless, those carriers that are present yield band like conduction with relatively high mobilities.

For insulators, the position of the Fermi level ϵ_F is ordinarily controlled by the defects and impurities in the material. In any event, for the case in which electrons dominate, the carrier concentration is given by:

$$n = N_c \exp [- (\epsilon_c - \epsilon_F) / K_B T] \dots\dots\dots (1-14)$$

Where N_c is the effective density of states in the conduction band and ϵ_c is the conduction band edge. The electrical conductivity is then $\sigma = ne\mu$ where the mobility μ is only a weak function of temperature.

The conductivity, however, rapidly increases with increasing temperature because $(\epsilon_c - \epsilon_F)$ in Eq. (1-14) is ordinarily very large. Analogous expressions involving $(\epsilon_F - \epsilon_v)$ are valid for the case in which holes predominate (1-15).

1-2-7-2- **Electrical Breakdown**

Since electrical isolation is one of the major commercial uses of insulators, their resistance to current flow at large applied fields is of the utmost importance. All insulators eventually conduct if a sufficiently large field is applied across them; this phenomena ordinarily occurs catastrophically and is called breakdown (1-16). There are several mechanisms for breakdown, all can be classified as either electronic or thermal. Electronic breakdown can be initiated by the excess kinetic energy that the conduction electrons obtain when the applied field accelerates them.

Eventually, these carriers move sufficiently fast to excite a bound electron across the gap, a phenomenon known as impact ionization. This increases the free-carrier concentration, and the field also accelerates the new carriers. Finally, a process entirely analogous to a nuclear chain reaction takes place resulting in a massive increase in free-carrier concentration known as a valence breakdown. A second important electronic mechanism for breakdown arises from the direct quantum mechanical tunneling of electrons across the gap induced by the applied field. At the critical value of field, the increasing in the carrier concentration induces what is called Zener breakdown (1-17).

Thermal breakdown is caused by the power dissipation ($I^2 R$) which occurs whenever a current passes through any material. This increases the temperature of the insulator; a phenomenon called Joule heating. But even a small temperature increase induces a large jump in the activated electrical conductivity, which in turn sharply increases the Joule heating. This positive feedback eventually leads to thermal runaway, a very rapid rise in the temperature of the insulator.

Both electronic and thermal breakdown are generally irreversible, permanently damaging this insulator.

1-2-1- **Electrical Conductivity of Semiconductors**

Semiconductors are defined as that class of non-metallic materials in which the electrical conductivity can be varied over many orders of magnitude in a controlled manner, for example, by changing the temperature, applying light or introducing chemical impurities. In every case, the concentration of free carriers is changed.

The importance of semiconductors has been made abundantly clear by the development of ever more sophisticated electronic devices. Beginning with the transistor in 1947. Nowadays up to 2×10^8 transistors can be routinely fabricated on a (1 cm^2) silicon chip making possible in expensive electronic equipment, computers, imaging systems, and a wide array of other devices. These devices will depend on the existence of materials whose electrical conductivity can be carefully controlled by the application of specific external sources of energy, such as electric field, light and heat. Metals are important for interconnections and insulators for isolation, but semiconductors are essential for the actual device operation.

Since a semiconductor must have its Fermi level within a gap, at least two bands must be important. The normally filled band below ϵ_F is called the valence band; the normally empty band above ϵ_F is called the conduction band. Any electron excited into the conduction band can contribute to the electrical conductivity. However, the absence of an electron from the nearly filled valence band also contributes to the conductivity. Since electrons near the bottom of a band always make a positive contribution, and yet a filled band yields zero net conductivity, electrons near the top of a band must make a negative contribution to conduction. Thus, the removal of such an electron must make a positive contribution. The absence of electrons near the top of a band is more easily looked

at as the presence of positively charged free carriers, known as holes ⁽¹¹⁸⁾. Under ideal conditions, a pure semiconductor contains equal densities of electrons in the conduction band and holes in the Valence band. In this case, both carrier types contribute to conductivity ⁽¹¹⁹⁾.

The electrical conductivity of semiconductor vanishes at $T = 0$ K because the Fermi level lies within a gap. At all other temperatures there will always be a finite concentration of electrons in the conduction band, n , and a finite concentration of holes in the valence band, P . For an intrinsic semiconductor, free carriers must be excited across the gap. In the absence of other sources of energy, only the thermal vibrations of the ion cores excite these carriers. Since the gap is much larger than $k_B T$, the electrical conductivity of an intrinsic semiconductor is relatively low, although it increases very rapidly with increasing temperature, in intrinsic semiconductor $g(\epsilon) = 0$. When a semiconductor is not intrinsic, which can only happen when $g(\epsilon) \neq 0$ within the gap.

Amorphous semiconductors differ from their crystalline counterparts primarily because of the absence of sharp band edges. Local bond length distortions and bond angle strains can lead to a tailing of $g(\epsilon)$ below ϵ_c and above ϵ_v . Those so-called band tails are expected to be a measure of the extent of the positional disorder in the solid. Recent evidence indicates that the band tails decay exponentially into the gap, with a characteristic energy related to the preparation temperature of the material. The band tail states affect the position of the Fermi level in amorphous semiconductors ⁽¹²⁰⁾.

1-2-1- The Energy Gap

The energy gap $[E_g]$ may be defined as the lowest energy to transform a charge carrier from the top of the valence band to the lowest bottom of the conduction band i.e. is the difference in energy between the highest point in the valence band the lowest point in the conduction band ^(121, 122). It represents one of an importance optical property of organic semiconductors ^(123, 124).

The variation of the concentration of the current carriers (electrons and holes) with temperature T can be expressed as follows :

$$\sigma = \sigma_0 \exp \left[- \frac{E_g}{2 K_B T} \right] \dots\dots\dots (1-18)$$

where K_B is Boltzmann's constant , and σ is the conductivity , T is absolute temperature . The factor $(1/2)$ in the exponent appears with intrinsic semiconductors because the possible distributions of electrons in the conduction band are independent of the distribution of holes in the valence band . If it is assumed that the mobility of the carrier varies rather slowly with temperature , Eq. (1-18) may be rewritten for the experimental conductivity as follows :

$$\sigma = \sigma_0 \exp \left[- \frac{E_{act}}{K_B T} \right] \dots\dots\dots (1-19)$$

Where $E_{act} = 1/2 E_g$. In this equation the energy term is one of the most important factors for the study of organic semiconductors .

The observed values of (E_g) are almost equal leading to further assumption that the molecular triplet state is involved in the conduction $(1-20)$. In organic crystals , the overlaps of molecular orbitals are generally very small . Therefore, it would be reasonable that the orbitals of molecule be isolated from that of others . Because of their isolation , any free electron formed may spend most of the time in the neighbor hood of molecule or another and very little time in the interstitial regions . A similar consideration applies also to free hole states . The carriers (electrons or holes) which spend along time at some molecule will jump to a neighbor's molecule by the perturbations arising from the presence of other molecules (hopping model) $(1-20)$.

To find the excitation energy for the lowest conducting state for the hopping model , the charge transfer mechanism is considered to occur in several steps . The electron is first removed

from its original molecular location to a point far from the crystal ; this requires the ionization energy . Bringing the electron back to the crystal and placing it on the second molecule involves the electron affinity energy . If the ion pair is widely separated each ion will polarize the surrounding molecules . The energy of interaction of each ion with the polarization is identical for the two ions .

Either the electrons on the negative ions or the hole left behind on the positive ions can carry current by hopping to adjacent molecules . The two charges are sufficiently far apart that they act independently of one another .

According to the correlated barrier hopping (CBH) model , the exponential factor , S , can be evaluated using equation (1-20)

$$S = \frac{d(\ln \sigma_{ac})}{d(\ln \omega)} = 1 - \frac{6K_B T}{W_m - K_B T \ln\left(\frac{1}{\omega \tau_o}\right)} \quad (1-20)$$

Where W_m is the maximum barrier height of the hopping process and $\left(\frac{1}{\tau_o}\right)$ is a photon frequency .

(Elliot , 1971) (1-21) suggested that :

$$E_g = W_m - K_B T \ln\left(\frac{1}{\omega \tau_o}\right) \quad (1-21)$$

therefore ; Eq. (1-20) becomes :

$$S = 1 - \frac{6K_B T}{E_g} \quad (1-22)$$

The correlation between the energy gap of organic solids and their chemical structures were studied . Eley and parfitt (1-23) studied a series of polycyclic aromatic differing in the number of condensed rings . It was found that the electrical resistivity and energy gap decreases with increase number of condensed aromatic rings (1-24) .

1-3- **Electrical Properties of Polymers**

The most familiar electrical property of polymers is their high resistance . The resistivity is an intrinsic material property which mainly depends on temperature , humidity and the nature of the polymer and its impurities ^(1.4) . The mode of conduction is usually ionic and is enhanced by humidity by several orders of magnitude .

Under AC electric fields , polymers store electrical energy proportional to their capacitance which depends on an intrinsic material property termed "dielectric constant , relative permittivity , or permittivity of free space" . Like resistivity , dielectric constant depends on conditions and the nature of the material . In addition to charge storage , polymers dissipate part of the AC electrical energy , as heat . The intrinsic material property that describes this process is the loss factor .

Coupling of the polymer motion to an electric field causes the electrical response of polymers . This coupling occurs in three principal ways ^(1.4) :

- 1- Polymerization : The polarization measures the ability of atoms to distort their normal electron configuration in response to an applied field . It depends on the nature of the atoms present increasing with increasing atom size , and is manifested in the optical and all lower – frequency responses .
- 2- Dipole interactions : Dipoles result from an asymmetric distribution of charge between nearby atoms . The viscous motion of the polymer chains in which the dipoles occur determines dipole motion in polymers .
- 3- Ionic interaction : Both free and attached ions to a polymer chain , also couple their motion to an applied . Free ions contribute to DC conduction in proportion to their concentration and mobility . Attached ions reflect the motion of the polymer chains to which they are bound .

1-3-1- **Electrically Conducting Polymers**

The unbeatable combination of characteristics such as ease of fabrication , low cost , high weight and excellent insulation properties have made polymers one of the most desirable materials

for electrical applications. Although, the majority of polymers applications involve using as insulator. Polymers can made conductivity by modifying the basic matrix with proper additives such as carbon – black or metal powders.

Typical electrical applications of polymeric materials as insulators include plastic – coated wires, terminals, connectors, industrial and house – hold plugs, and printed circuit boards. The following requirements are essential for insulator application (1.1):

- 1- The insulators must have high enough dielectric strength to withstand the electrical field between the conductors.
- 2- The insulator must possess good (arc) resistance to prevent damage in case of arcing and to prevent leakage of current across the conductors.
- 3- An insulator must maintain integrity under a wide variety environmental hazards such as humidity, temperature and radiation.
- 4- An insulating must be mechanically strong enough to resist vibration shocks and other mechanical forces.

Polymers are commonly used as non – conducting materials (insulators) which has conductivity varies between $10^{-10} - 10^{-14} \text{ S. cm}^{-1}$ enable polymers to be used as insulators.

The Conductivity of conductor such as copper (conductivity $0.6 \times 10^9 \text{ S. cm}^{-1}$) is due to electron availability to transmit the current when an electrical potential is applied (1.2). While the polymeric materials are insulators, because they have no free electrons and consist covalent bonds which usually passes very weak current when direct voltage is applied. Polymers are classified from insulating point of view to:

- 1- Polar polymers which have relatively higher conductivity such as polycarbonat, nylon.
- 2- Non – polar polymers which are essentially non – conductive such as polyethylene, polystyrene, and polyformaldehyde.

Several type of thermosets have been utilized in electric and electronic application, familiar used include cable sheeting; dielectric layers; films printed circuit substraters and a semi – conductor encapsulates (1.3).

Some progresses have been achieved in obtaining conductive or semi conductive thermosets . Thus several phenolic structures have been crosslinked via cyanate group forming thermosets with conductivity of $(1 \cdot 10^{-4} \text{ S. cm}^{-1})$ (111).

Table (1-2) shows some conductor and semiconductor .polymers with structures .

Table (1-2) Some polymers with their electrical conductivity and energy

gap (111)

Names of polymers	Chemical Structure	Electrical Conductivity (ohm/cm) (Energy gap e.V)
Polypyrrole		$10^2 - 10^3$ ($E_g = 3 \text{ eV}$)
polythiophen		10^2 ($E_g = 2.7 \text{ eV}$)
Polyphenyl		10^3 ($E_g = 3.5 \text{ eV}$)
polyaniline		$10^2 - 10^3$
polystyrene		10^3
polyvinyl		$10^3 - 10^6$
polythionitroso		$10^3 - 10^5$

Number of Polymers are well known , which have highly conjugated structures including polyacetylene and polypyrrole .These can be doped to exhibit electrical conductivity approach to those of metals . Poly (P- phenylene) can be doped to give high conductivity and this leads to the development of a number of conducting polymer system that based on molecules containing aromatic rings . A wide range of compounds have been used as dopant in these systems , such as ; $[A_0F_0, I_2, SbF_6, AlCl_3, ZnCl_2, IF_5, MoCl_5 \text{ and } WC_6]$ (112).

The conductivity induced within these materials varies over several orders of magnitude (Typically between 10^{-11} to 10^7 ohm/cm) and can be controlled by the quantity of doping . These materials frequently belong to the class of polyaromatic polymers .

Conducting polymers find applications in the area of Radar Cross Section (RCS), reduction and electromagnetic shielding . The flexibility and controllability of the doping levels added an attraction since the conduction polymers can be tailro made for specific Radar Absorbing Materiel (RAM). Conducting polymers such as polypyrrolle , polyaniline and polyacrylthiophenes have been reported in the literature as materials in the fabrication of RAM ⁽¹¹³⁾ .

Experimetal studies indicated doped polyacetylene may be useful in application such as the replacement of increasingly scars conventional conductors ; low – cost solar photovoltaic materials ; and light weight high – energy – density batteries ⁽¹¹³⁾ .

Successful doping has been achieved using avariety of other conjugated polymers . It appear that a large number of conjugate polymers might be semiconductors and might be capable of charge transfer doping .

1-3-2- **The Electrical Conductivity (DC)**

Electrical conductivity is a material property which has the largest variation in its Value ⁽¹¹⁴⁾ . Recently , conducting as well as semiconducting polymers have been widely produced . Table (1-3) shows the electrical conductivity of metals , semiconductors and insulators .

Table (1-3) Typical values of conductivity for metals , semiconductors and insulators ⁽¹¹⁵⁾

Class of Substance	Typical Values for Conductivity (ohm cm) ⁻¹
--------------------	---

Conductors	$10^7 - 10^8$
Inorganic semiconductors	$10^{-9} - 10^3$
Organic semiconductors	$10^{-14} - 10^2$
Insulators	Below 10^{-14}

Figure (1-4) shows the range of electrical conductivity of such material.

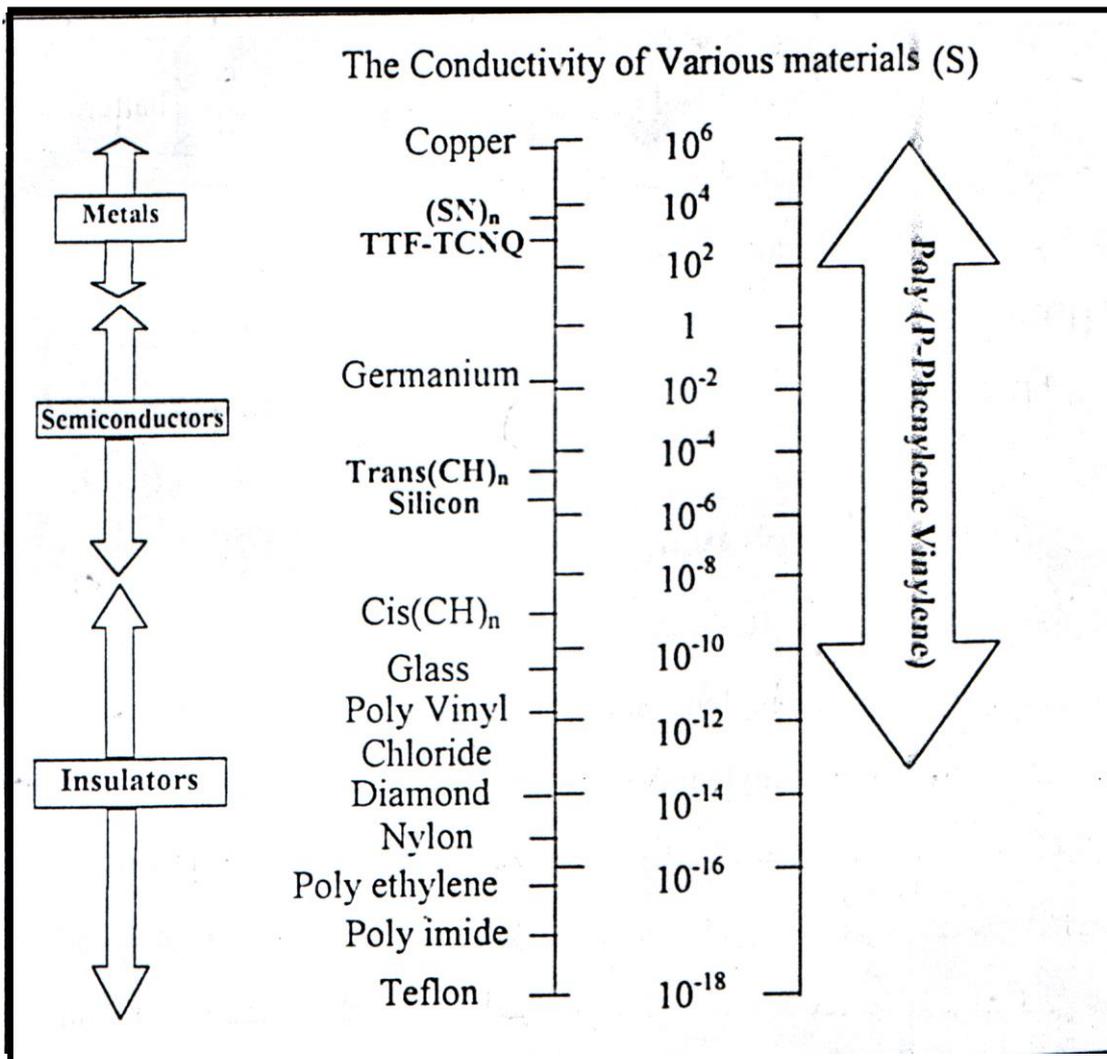


Fig. (1-ξ) The electrical conductivity of materials (11ξ) .

Dielectric or electrical insulating materials are understood as those materials in which electrostatic field can persist for longtime . Such materials offer a very resistance to the passage of electric current under the action of the direct applied voltage . Therefore , these materials are greatly different in their basic electrical properties from conductive materials . The resistivity of these insulating materials should be infinitely high ; and hence they should not carry a current under the action of direct – voltage .

For a body with constant cross section A and length l (Thickness) , the volume resistivity (ρ) can be found from the elementary formula (113) :

$$\rho = R \frac{A}{l} \quad (1-23)$$

Or the conductivity σ is

$$\sigma = \frac{1}{\rho} = \frac{l}{RA} \quad (1-24)$$

Where R is the Volume resistance of the material . The unit of σ , is $(\text{ohm cm})^{-1}$. The resistivity is equal to the reciprocal of conductivity , $(\sigma = \frac{1}{\rho})$.

As for semiconductors and insulators , they are effected by temperature because they have a negative thermal coefficient , which means that their resistance decreases exponentially with increases of temperature ⁽¹⁻²⁵⁾ . The change of electrical conductivity with change of temperature is subject to Arrhenius equation ⁽¹⁻²⁶⁾ . which is given by Eq. (1-19) .

$$\left[\sigma = \sigma_0 \exp \left[- \frac{E_{\text{act}}}{K_B T} \right] \right] \dots\dots\dots (1-19)$$

Where σ is the electrical conductivity and σ_0 represent metallic conductivity , which is constant , and depend on temperature .

1-3-3- **The Activation Energy**

The activation energy is physical transformation of a solid or liquid or a chemical reaction really involves the rearrangement of agroup of atoms into a new or more stable configuration . To accomplish this configuration , the reactions or the deformed atoms must be activated to a state of higher energy before the process can occur spontaneously . The smallest energy that will raise the

free energy of an atom or a molecule to such a state so that it can go over the energy barrier is called the activation energy $(1-19)$. This corresponds to the top of the energy barrier.

The rate of the process is dependent on the number of molecules or particles having sufficient thermal energy to reach the energy barrier and on the velocity with which these molecules or atoms will cross this energy barrier. A fraction of atoms or molecules acquiring sufficient energy to surmount the potential barrier will be proportional to the factor $[\exp(E_{act}/K_B T)]$, where, E_{act} , is the activation energy; K_B , is the Boltzmann constant; and T , is the absolute temperature. The activation energy can be calculated using Arrhenius equation $(1-19)$. Plot the logarithm of the conductivity versus the reciprocal of the absolute temperature is a straight line and from its slope an apparent energy of activation, E_{act} , for the process can be calculated.

1-2-4- The Electrical Conductivity (AC)

The measurements of AC conductivity are considered complementary the measurements of DC conductivity. They can not substitute due to the limitation of DC conductivity and their inability to explain the conductivity mechanism accurately. So, the measurements of AC conductivity and DC conductivity gave a clear and complete view of the electrical properties for materials. It is also important in giving information about the response of the system to polarization, and the loss regions due to the applied alternative field. It is useful in organic semiconductor to obtain the amount of loss that results from the rotation of dipole moment with the group of atoms in molecule. Some organic materials are characterized with loss of AC current, which is not related to continuous internal resistance or the conductivity of bulk materials, but this is due to impurities, which are not effective in case of DC conduction.

The behaviour of semiconductors is based on the reliance of their electrical conductivity upon electric field and applied voltage where conductivity increases with the frequency increase according to the following equation $(1-20)$.

$$\sigma_{ac} = A\omega^S \quad (1-20)$$

Where, A is a constant and S represent the exponential factor.

1-4- Polarization

The degree to which a material response to an applied electric field can be most easily appreciated in the case of parallel capacitor, The fixed voltage (V) is applied across such capacitor, where the plates are separated by distance (d) in Vacuum, as shown in Fig. (1-9a), the electric field in the region between the plates, having a magnitude (1-9):

$$\bar{E} = V/d \dots\dots\dots (1-26)$$

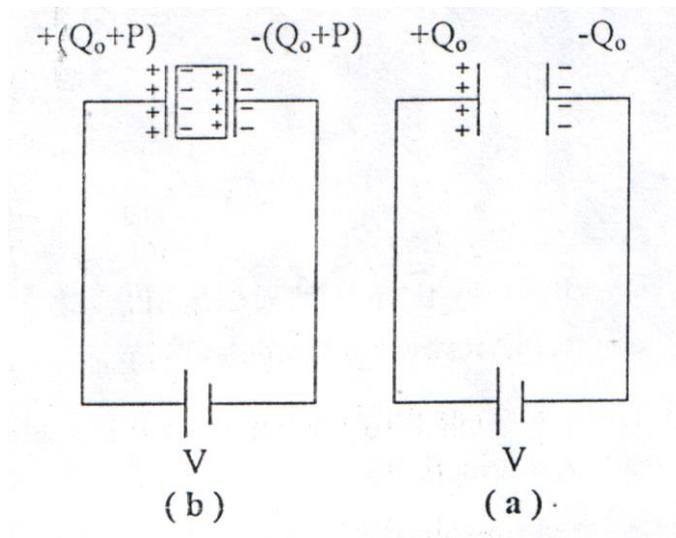


Fig. (1-9) Charges on parallel – plate Capacitor with :

- a- Vacuum between the plates .
- b- A dielectric between the plates .

Where the field is necessarily perpendicular to plates, it follows from Coulombs law i.e., the Charges (+Q) per unit area stored on the plates are directly proportional to the magnitude of the field (1-10):

$$Q = \epsilon_0 \bar{E} \dots\dots\dots (1-27)$$

Where ϵ_0 : Permittivity of free space and has value of $8.85 \times 10^{-12} \text{ F.M}^{-1}$.

The Vacuum capacitance per unit area of electrode (C_0) is defined as ,

$$C_0 = \frac{Q}{V} = \frac{\text{stored charge per unit electrode area}}{\text{Applied Voltage}} \dots\dots\dots (1-28)$$

When considering the capacitors with materials of interest between their plates , as shown in Fig. (1-9b) . The materials will response to the applied electric field by redistributing its component charges to some extent . Positive charge being attracted toward the negative electrode and vice versa , the effect is called polarization of the material .

The polarization (P) is thus defined as a vector quantity expressing the magnitude and direction of electric moment per unit volume induced in the material by the applied field . Each volume element of polarized material will behave electrically as its consisted of charge (+q) and (-q) separated by distance (l) in the field direction giving adipole moment .

$$q l = p dV .$$

These dipoles will combine in an analogous manner as head – to – tail adding magnets to produce apolarization charge (+P) and (-P) per unit area on the surface adjacent to the electrodes .

The presence of these polarization or bounded charges can be stored on the capacitor electrodes for the same applied voltage and the capacitance of the system is there by increased :

$$\epsilon = \frac{C}{C_0} = \frac{Q + P}{Q} \dots\dots\dots (1-29)$$

Where ϵ : commonly called the permittivity of the material :

Substituting the value of Q from equation (1-27) in to the equation (1-29) , the resulting polarization is given by (1-30) :

$$P = (\epsilon - 1) \epsilon_0 \bar{E} \quad (1-30)$$

The quantity $(\epsilon \epsilon_0 \bar{E})$ is called the electric displacement of the material (\bar{D}), which can be represented as

$$\bar{D} = \epsilon \epsilon_0 \bar{E} = \epsilon_0 \bar{E} + \bar{P} \quad (1-31)$$

This is the fundamental electric field equation , which applied at any point in an isotropic medium .

In polar materials some kinds of polarization occur , varying from frequency region to another , as inter facial , polar , atomic and electronic polarization as shown in fig. (1-6) .

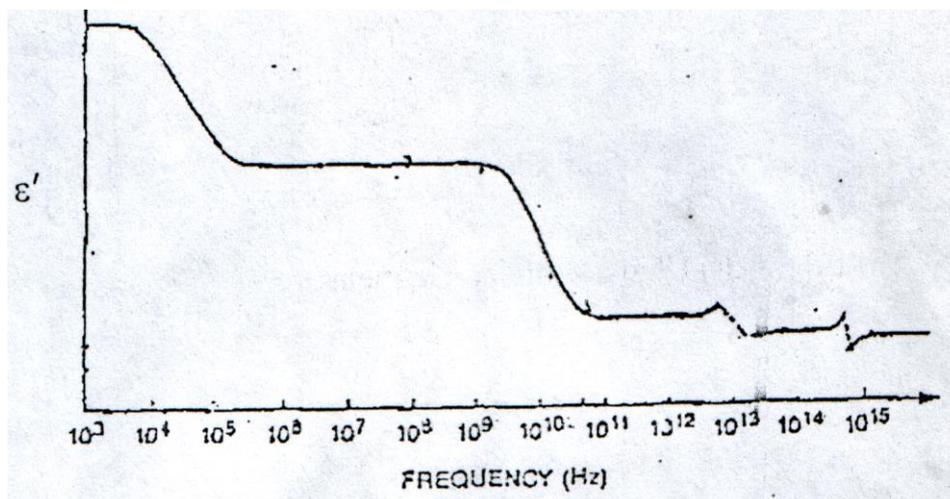


Fig. (1-6) Types of polarization

The interfacial polarization occurs at low frequency , and caused by the alternating accumulation of charge interface between different phases of the polymer , known as Maxwell – Wanger polarization .

At high frequencies the peak of the loss factor is caused by the dipole polarization, the dipole polarization is caused by the rotational displacement of molecular dipole under the influence of alternating electronic field. There is other two types of polarization, atomic and electronic polarization which occur at higher frequencies (1¹², 1¹³).

1-2- Techniques Used in Measuring Dielectric Properties

The electrical measurements can be made over a wide range of frequencies with a high degree of precision. Thus the dielectric constant and loss of solid polymers often known from 10⁻⁴ Hz up to optical frequencies. The methods which are appropriate for the various frequency regions are summarized as follow [Fig. (1-7) (1¹⁴, 1¹⁵)].

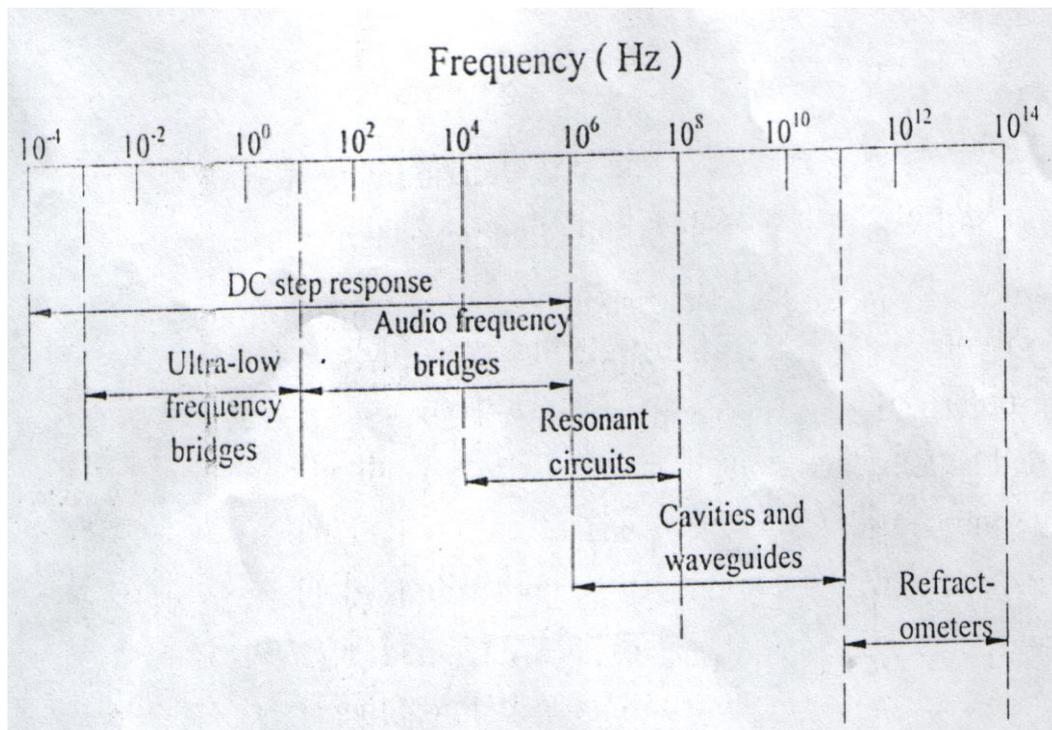


Fig. (1-7) summary of dielectric measurements methods

1-2-1- Distributed – Circuit Method

This method are always used at high frequencies (> 10⁶ Hz) where the electromagnetic wavelength inevitably becomes comparable with sample dimensions. The sample become the

medium for propagation of electromagnetic wave . Dielectric constant and loss must then be obtained from the observed and attenuation characteristics .

1-2-2 Lumped – Circuit Method

The Lumped – Circuit method are always used at lower frequencies ($< 10^8$ Hz) . This method is used to determine the equivalent electrical of the specimen at given frequency . The low components of the complex permittivity of the materials can be expressed in terms of equivalent parallel circuit , represented by capacitance (CP) in parallel with resistance (RP) , or alternatively , the specimen may be regarded in terms of series circuit as shown in Fig. (1-1) .

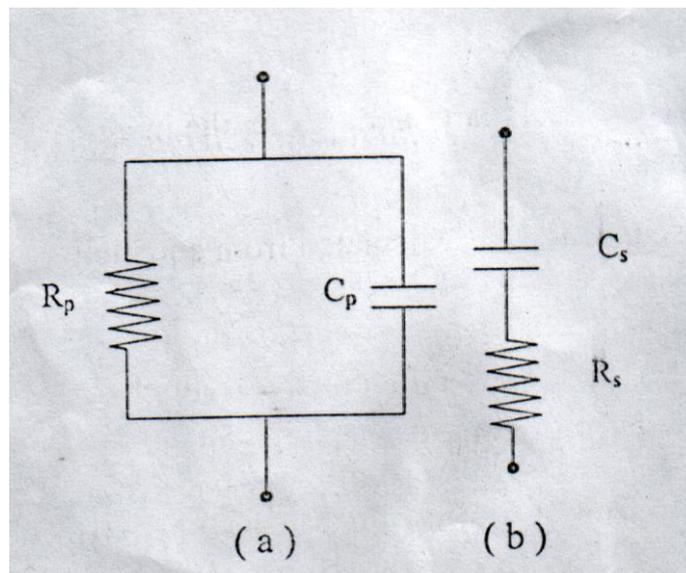


Fig. (1-1) Equivalent electrical circuit of dielectric specimen :

a- Parallel , b- Series

Therefore , we can calculate the dielectric constant and loss of the material from measured values of the equivalent parallel or series circuit components of the specimen .

The permittivity values were calculated from measured values of the capacitance (CP) relatively to capacitance of the electrode (1-23) .

$$\epsilon' = \frac{C_p}{C_0} \quad (1-32)$$

$$\epsilon'' = \frac{1}{R_p C_0 \omega} \quad (1-33)$$

$$\text{And } \tan \delta = \frac{\epsilon''}{\epsilon'} = \frac{\text{energy dissipated per cycle}}{\text{energy stored per cycle}} = \frac{1}{R_p C_p \omega} \quad (1-34)$$

Where :

ϵ'' is called the dielectric loss factor

$\tan \delta$ is called the loss tangent , defined as the ratio of power dissipation to the reactive power .

the complex dielectric constant ϵ^* can be written as ,

$$\epsilon^* = \epsilon' - i\epsilon'' \quad (1-35)$$

Where , ϵ' is the real part , and ϵ'' is the imaginary part of the complex dielectric constant .

The resistance R_p is calculated from equation :

$$\frac{1}{Z} = \frac{1}{R_p} + i\omega C_p \quad (1-36)$$

Where , Z is the total impedance .

The reciprocal of specimen resistance in equivalent parallel circuit for a given frequency is sometime called the AC conductance (G_p) , it is combination of DC conductance , by which we mean

any real flow of charge through the sample under the influence of the applied field , and the anomalous conductance due to any time – dependent polarization processes .

$$G_p = \frac{1}{R_p} \quad (1-37)$$

The contribution that a true DC conductivity (γ_a) (conductivity is defined as the reciprocal of resistivity which is the resistance between opposite faces of a unit cube of material) will make to the dielectric loss at angular frequency can be readily calculated as follows for the materials in parallel – plate capacitor , substituting equation (1-37) into (1-33) ,

$$\epsilon'' = \frac{G_p}{C_o \omega}$$

$$\text{and } C_o = \frac{\epsilon_o A}{d}$$

A ; area of capacitor

b- distance between the plate of capacitor .

$$G_p = \frac{\gamma_a A}{d}$$

Where γ_a active conductivity ,and hence,

$$\epsilon'' = \frac{\gamma_a}{\epsilon_o \omega} \quad (1-38)^{125,126}$$

1-7- **The Electrical Conductivity of Materials Ranges**

The electrical conductivity of pure polymers typically ranges between 10^{-17} and 10^{-14} S/cm . Typical electrical conductivity values are 10^5 S/cm for carbon black , 10^6 S/cm for graphite and 10^7 S/cm for aluminum (127) .

By embedding conductive fillers in polymers , materials can be designed with specific properties tailored to each application . In order to use the composite materials for conductive

applications, the materials should have an electrical conductivity in the range of 10^{-12} and 10^{-8} S/cm for electrostatic dissipation applications, 10^{-8} to 10^{-2} S/cm for moderately conductive applications and 10^{-2} S/cm and higher for shielding applications (Vijayalakshmi).

1-7- Effects of Multi – Filler Combination

An intensive works have been carried out in this field by varying the amount of single conductive filler in a composite materials (Srinivas). In comparison, limited work has been carried out dealing with the effect of combinations of different types of conductive fillers such as carbon black and graphite on the electrical conductivity of conductive composites.

Table (1-5) shows the electrical conductivity (σ) for nylon – 6, 6 composed with high quality milled synthetic graphite (Thermocarb Specialty Graphite) (Srinivas), electrically conductive carbon black and polyacrylonitrile (PAN) based carbon fiber.

Table (1-5) The effect of composite constituents on the conductivity of Nylon – 6, 6

Components	WT %	σ (S / cm)
Nylon – 6, 6	100	1.7×10^{-17}
Carbon black	0	
Graphite	10	
Carbon fiber	10	
Nylon – 6, 6	90	10^{-13}
Carbon black	0	
Nylon – 6, 6	90	10^{-12}
Graphit	10	
Nylon – 6, 6	90	10^{-12}
Carbon fiber	10	
Nylon – 6, 6	100	1.7×10^{-17}

Table (1-9) show the electrical conductivity of nylon – 6,6 polymer matrix composed with carbon black , milled graphite and carbon fiber⁽¹³⁾.

Table (1-9) the electrical conductivity of nylon – 6,6 composite consisting different composite ratios

Components	Wt%	σ (S / cm)
Nylon – 6,6	100	1.07×10^{-17}
Nylon – 6,6 Carbon black	90 0	1.28×10^{-7}
Nylon – 6,6 Graphite	70 30	8.01×10^{-8}
Nylon – 6,6 Carbon black Graphite	60 0 30	1.10×10^{-7}
Nylon – 6,6 Carbon fiber	80 20	7×10^{-10}
Nylon – 6,6 Carbon black Carbon fiber	70 0 20	0.37×10^{-7}
Nylon – 6,6 Graphite Carbon fiber	50 30 20	3.00×10^{-7}
Nylon – 6,6 Carbon black Graphite Carbon fiber	40 0 30 20	3.09

It has been reported that the conductivity of glassy polymers can be changed remarkably via composite technology , Thus the electrical conductivity for polycarbonate composed with carbon black , Milled graphite and carbon fiber was studied extensively , Representative data are shown in table (1-6) (13).

Table (1-6) the electrical conductivity of polycarbonate as a function of its composite composition

Components	Wt%	σ (S / cm)
Polycarbonate	100	6.92×10^{-18}
Polycarbonate Carbon black	90 0	4.37×10^{-7}
Polycarbonate Graphite	70 30	9.00×10^{-7}
Polycarbonate Carbon black Graphite	60 0 30	1.87×10^{-1}
Polycarbonate Carbon fiber	80 20	2.73×10^{-7}
Polycarbonate Carbon black Carbon fiber	70 0 20	3.00×10^{-1}
Polycarbonate Graphite Carbon fiber	50 30 20	9.33×10^{-7}
Polycarbonate Carbon black Graphite Carbon fiber	40 0 30 20	1.41

Other investigators have shown that graphite filler at (30% w/w) used alone with polyethylene to produce a composite with electrical conductivity of 10^{-5} S/cm (132). Similar effect of carbon black and graphite on the conductivity of polyacetal and polyamide has also been noticed (13,133).

1-1- Hydrogel Polymers

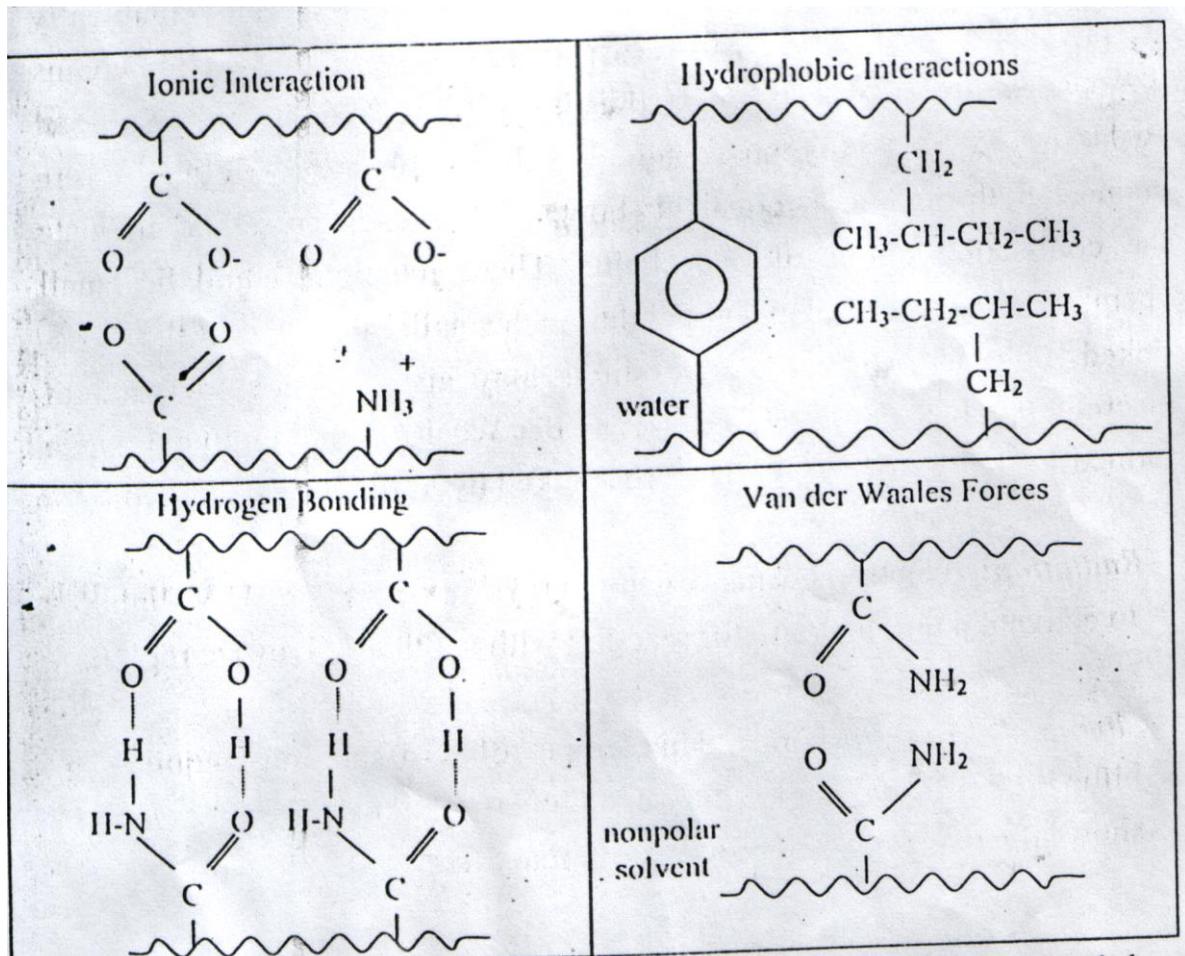
Hydrogel is a three – dimensional network of hydrophilic polymers in which large amount of water is present , Which swell in water without dissolving. In general, the amount of water is at least (90% w/w)of the total weight (134-136) . If water is composed of more than (90% w/w)of the total weight , The hydrogel is called " Superabsorbent " (137) . The most characteristic property of hydrogel is that it swells in the presence of water and shrink in the absence of water (138) . The dried hydrogel (xerogel) becomes much smaller in size than the swollen hydrogel .

Polymer chains of hydrogel are usually crosslinked either chemically or physically . In the chemically crosslinked hydrogel , The polymer chains are connected by covalent bonds , Thus it is difficult to change the shape of such gels while polymer chain , Which are physically intanged are connected through non covalent bonds (139) . The term " Crosslink " indicate the connection points of two chains . These junctions could be small chemical bridges of molecular weight much smaller than that of the crosslinked polymer chains . A crosslinks may also be an association of macromolecular chains caused by forces or an aggregate formed via hydrogen bonds . The crosslinked hydrogel can be formed by :

- 1- Radiation : using electron beams (140) , gamm arays (141) x – rays (142) , or U.V. light (143) to activate a polymer site for reaction with another polymeric region .
- 2- Chemical crosslinking : This type of crosslinking requires a bi-functional , low molecular weight crosslinking agent (144) .

Polymers with other functional group can also be crosslinked by other chemical reactions . for example , Albumin and gelatin can be crosslinked with aldehyde (140,147) . Some hydrogels are formed by physical interaction between polymer chains . These interactions include hydrogen bonding , VanDer Waales interactions , ionic and hydrophobic interactions (139) as shown in Fig.(1-9)

Fig (1-9) the major four types of interaction forces which control the behaviour of most responsive gels .



1-9- Classification of Physical Gels :

- 1- Blend hydrogels .
- 2- IPN and semi – IPN hydrogels .
- 3- Block copolymer hydrogels .
- 4- Poly electrolyte complex hydrogels .
- 5- Counter ion induced hydrogels .
- 6- Thermally induced hydrogel .

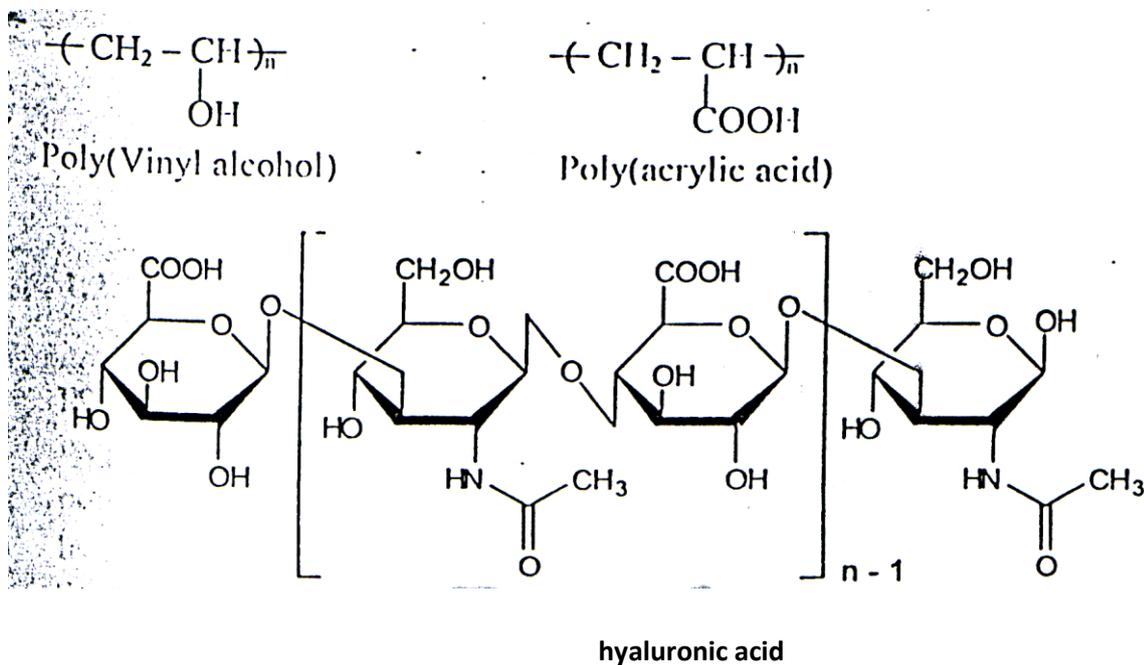
Y- Specific interaction induced hydrogels .

1- 4 - 1- **Blend Hydrogels :**

Blend hydrogels are usually prepared by solvent casting or precipitation from two different polymer solutions or more . The blend hydrogels normally have properties different from the hydrogels made from individual polymers . The hydrogels prepared in this way should consist at least one hydrophilic polymer to provide the water absorbing property , e.g. poly (ethylene oxide) – poly (propylene oxide) – poly (ethylene oxide)

(PEO – PPO - PEO) block copolymers were blended with poly lactic acid

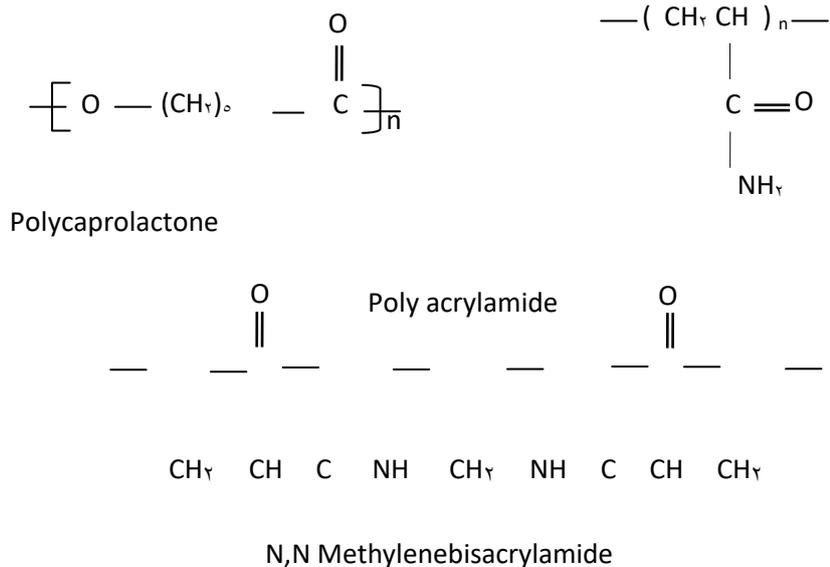
(PLA) to make hydrogels (144) . Other hydrogels were prepared by blending , Chitosan with poly (ethylene oxide) (149) , Chitosan and poly (vinyl alcohol) blend hydrogels was also prepared by solvent casting (150) . Hyaluronic acid was blended with poly (Acrylic acid) or poly (vinyl alcohol) to make hydrogels (151) .



1- 4- 2- **IPN and Semi IPN Gels :**

Another types of physical gels are IPN or semi – IPN .IPNs are any materials containing two different type of polymers , In a network form . In semi – IPNs only one of the components exists as net work

and is usually formed in the presence of the other components^(152,154). IPNs and semi – IPNs of poly (hydroxyl-ethylmethacrylate) (PHEMA) and poly (Caprolactone (PCL)) were prepared^(155,157). Carboxy ethyl cellulose was mixed with gelatin which was then crosslinked by glutaraldehyde to make semi – IPNs⁽¹⁵⁸⁾. IPNs were prepared by crosslinking gelatin with glutaraldehyde and acrylamide with N,N – M ethylene bisacrylamide⁽¹⁵⁹⁾.

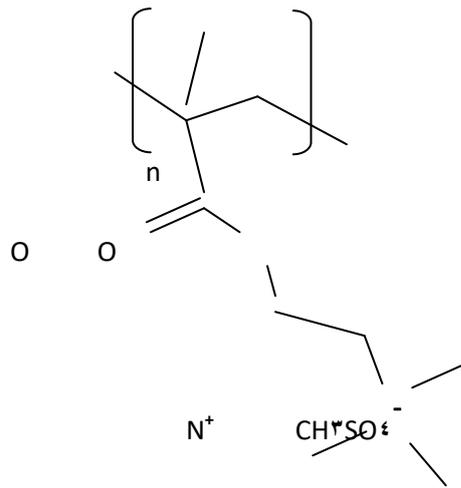


1-4-3- Block Copolymer Gels :

The physical gels can also be prepared from block copolymers , Thus poly (ethylene oxide) – Poly (lactic acid) block copolymer , Poly (ethylene oxide) – Poly (glycolic acid) block copolymers and Poly (ethylene oxide) – Poly (caprolactone) block copolymere are examples for this type of hydrogels^(160,162).

1-4-4- Poly Electrolytic Gels

Some hydrogels are made from poly salt or Poly electrolyte Complexes. Ionic interactions between two oppositely charged poly electrolytes lead to the formation of poly electrolyte complexes which swell in water . The examples for this type of gels are poly electrolyte film of amino group – containing chitosan with sodium alginate⁽¹⁶³⁾ , poly (methacryloyl ethyltrimethylammonium methyl sulphate) (PMETMMS)^(164,165).



PMETMMS

1-9-2- Counter Ion Induced Hydrogels

Certain polyelectrolytes can form hydrogels in the presence of counter ions . Typical example is sodium alginate which from gels in the presence of Ca^{2+} (166, 167) and the electrolyte consists of lithium perchlorate dissolved in ethylene carbonate solution immobilized with poly (methyl methacrylate) (168).

1-9-3- Thermally Induced Hydrogels

This type of gel is formed when thermal energy induce the structural change of polymer in solution or change the balance between hydrogen bonding and hydrophobic interaction . The good

examples for this class are , The gelatin of gelatin solution as temperature is lowered (169) and agarose gels can also be prepared by this method (171).

1- 4- 1- **Specific Interaction Induced Gels :**

Polymer networks can be formed by specific interactions such as interactions between glucose and concanavalin A (171, 172).

1- 1- **Environment – Sensitive Hydrogels**

One of the inherent properties of hydrogels is thier ability to swell in the presence of water and to shrink in the absence water (173). This property is common to all hydrogels with additional functions , Such ability to swell or shrink in response to asignal . These hydrogels are called " Smart hydrogels " (173). The most widely known smart hydrogels are those which response (i.e either swell , shrink , bend or degrade) due to the change in the environmental conditions , for this reason , they are usually known as environment- sensitive hydrogels . These hydrogels undergoes changes in their swelling ratio (which is the volume of the swollen hydrogel divided by the volume of the died hydrogel) rather abruptly upon small changes in the environmental parameters .

Table (1- 7) lists some environmental factors which affect the gel causes dramatic change in volume (174-175).

Table (1- 7) : Factors affecting gel characteristics which cause volume collapse .

Factor	Reference
1- pH	176 , 177
2- Temperature	178 , 179
3- Electric field	180-182
ξ - Ionic strength	183
ο - Salt type	184 , 185

γ - Solvent	۱۸۶
ν - Stress	۱۸۷, ۱۸۸
λ - Light	۱۸۹
ρ - Pressure	۱۹۰

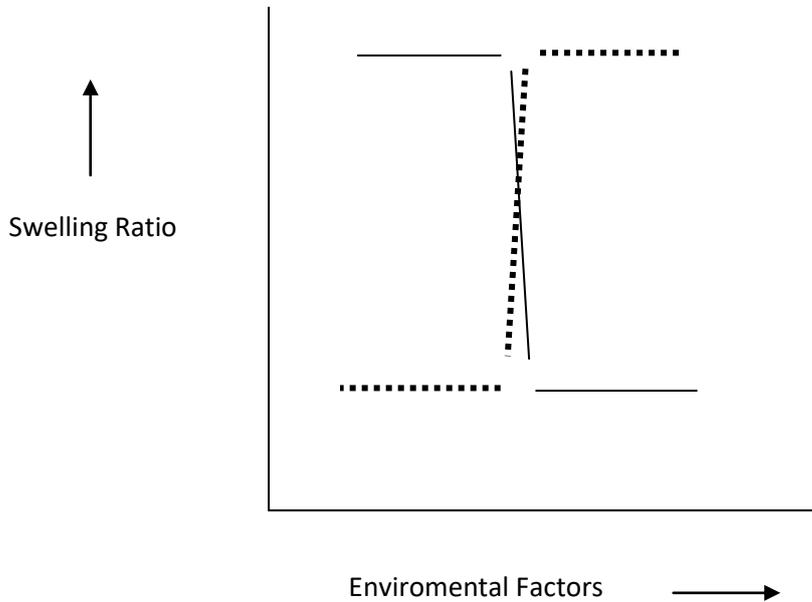
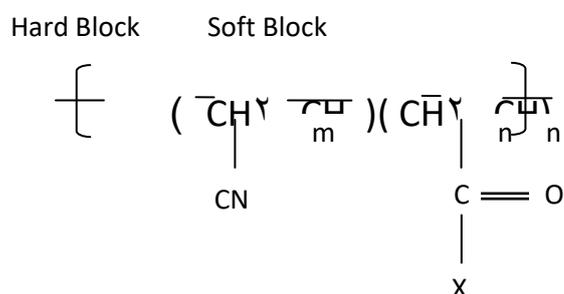


Fig. (۱-۱۰) Volume collapse of smart hydrogels in response to a small change in environmental factors . Hydrogels may undergo dramatic increase (dotted line) or decrease (solid line) in the swelling ratio .

۱-۱۱- Thermoplastic Hydrogels

Thermoplastic hydrogels are based on linear copolymers of hydrophilic and hydrophobic monomers . The hydrophilic monomers are called " Soft block " and the hydrophobic monomers are called " hard block " . The gel is formed by hydrophobic-hydrophobic interactions between chains of the copolymers (۱۹۱) .



✕ { NH₂ , O , -OH ,etc.....}

Thermoplastic hydrogels dissolve in organic solvent , which they only swell without dissolving in waters , and this property provides an advantage of easy processibility . Vinyl – γ – Pyrrolidone and methyl methacrylate are known to form thermoplastic hydrogels which have useful properties such as melt –processibility⁽¹⁹²⁾ .

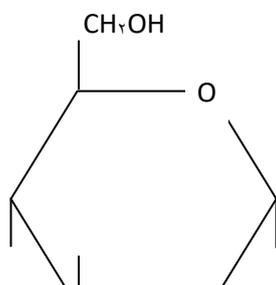
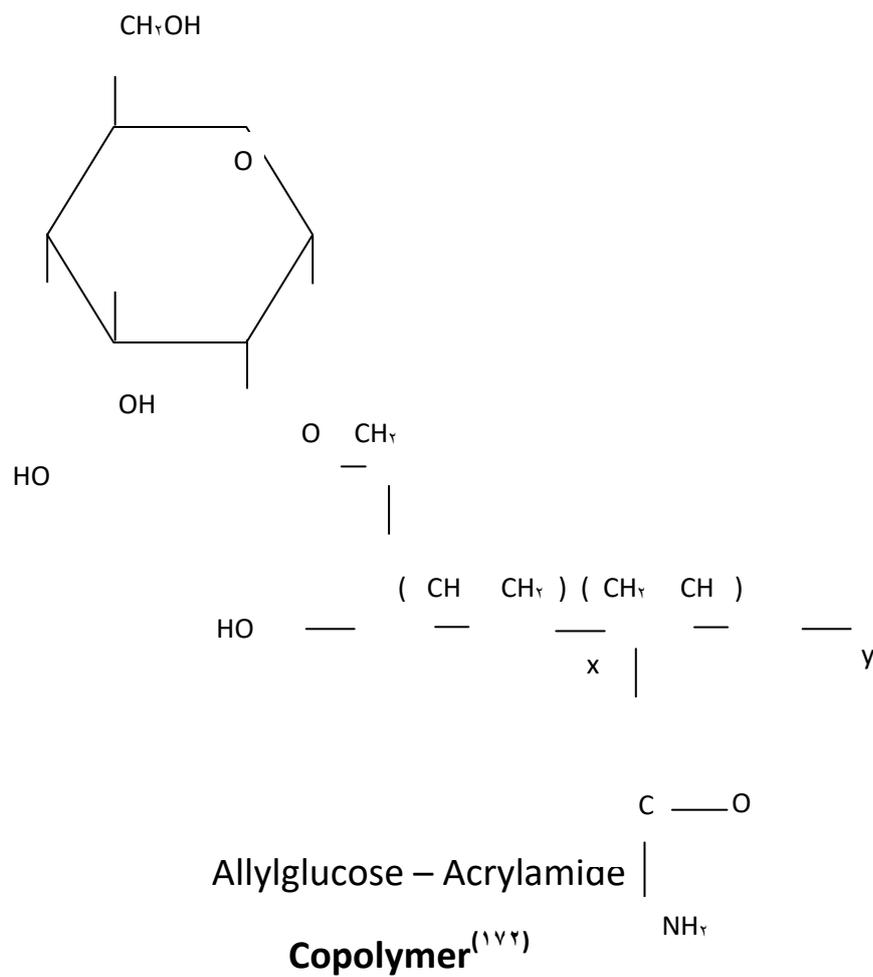
1- 12- **Hydrogel Foams**

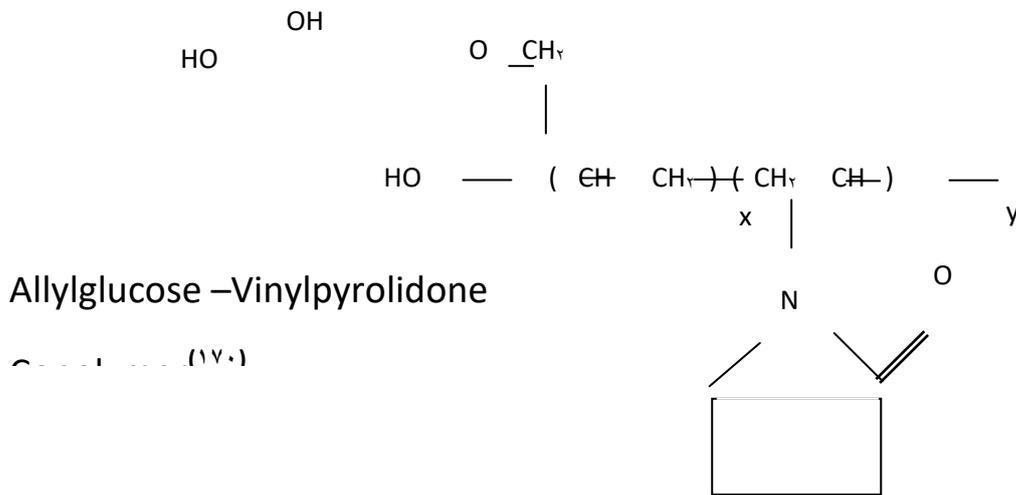
While hydrogels swell to a large extent in water , the equilibrium swelling usually takes along time from several hours to couple of days depending on the size and shape of the hydrogels . Hydrogel foams were recently developed^(193, 194) which are made by synthesizing the hydrogels in the presence of blowing a gent . The hydrogel foams prepared with macroscopic gas cells are different from hydrogel spongs⁽¹⁹⁵⁾ or macroporous hydrogels^(196, 197) . The size of pores in the hydrogel foams is orders of magnitude larger than the pore size (which is typically a few micrometers) in hydrogel spongs or macroporous hydrogels . In addition , the kinetics and the extent of swelling of hydrogel foams are much faster and larger than others⁽¹⁹⁸⁾ .

1- 13- **Ligand – Specific sol – gel phase – Reversible Hydrogels**

Physical gels are capable of undergoing Sol – Gel phase transition due to non – Covalent crosslinking of polymer chains . For example , hydrogels which become sol in the presence of glucose

were developed (1991). A high specific interaction between glucose and concanavalin A (Con A) was used to form physical crosslinks between glucose – containing polymer chains. The glucose molecules which are attached to the polymer backbone react with (Con A), and since the non – Covalent interactions between glucose and (Con A), the crosslinks formed are reversible.





The gel is formed by mixing glucose – containing polymers with Con. nA .

Upon addition of free glucose molecules , the hydrogel dissolves to become a sol owing to the detachment of polymer chains from Con A as a result of Competitive binding of the free glucose to Con A . The sol can become a gel again upon removal of free glucose . This concept is illustrated in Fig. (1-11) (197, 198, 199) .

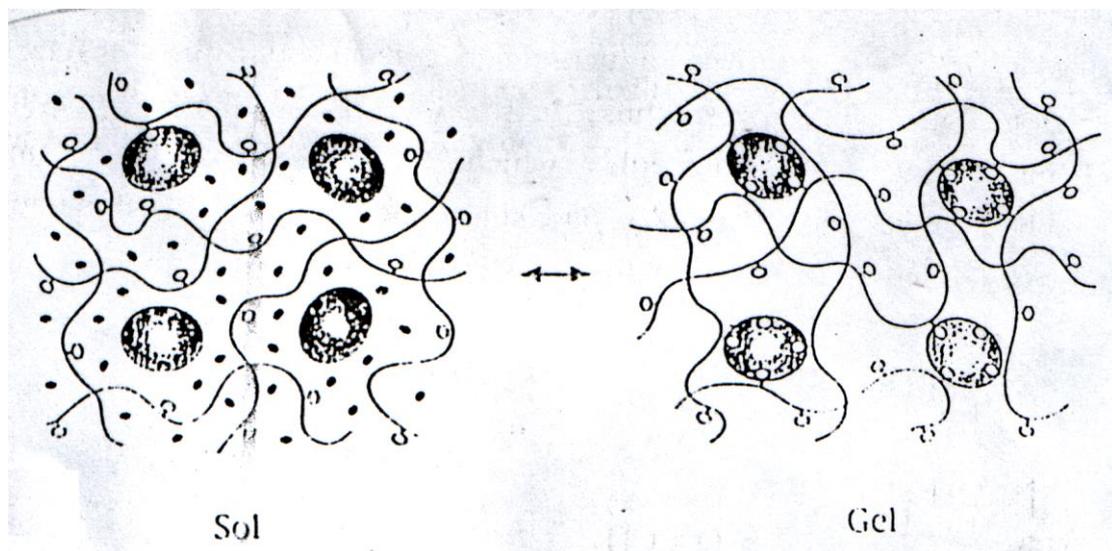


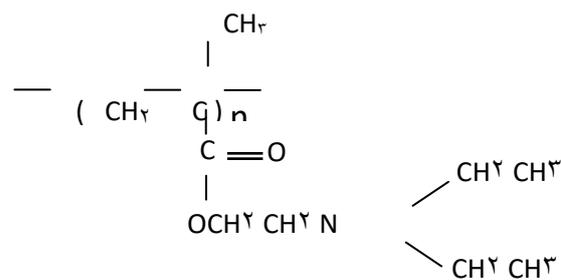
Fig. (1-11) : Sol – Gel phase transition . Large circles represent Con A molecules , small open hexagones represent glucose attached to the polymer chain and small closed hexagon represent free glucose .

There are many ligands with specific interactions such as antigen antibody⁽¹⁹⁹⁾.

1-14- Applications of hydrogels .

1-14-1- Pharmaceutical applications .

Much of the research on hydrogels have been focused on the application in controlled drug delivery system⁽¹⁹⁹⁻²⁰³⁾. The most widely used example is the delivery of insulin . Temporal control of insulin delivery can be achieved by utilization of smart hydrogels which release more insulin in response to increase in glucose level . These hydrogel systems are made of PH-Sensitive polymers such as poly (Diethylamino ethylmethacrylate) (PDEAEMA)⁽²⁰⁴⁾ or made of thermo – sensitive hydrogels which are usually consist polyacrylamide derivatives with hydrophobic groups⁽²⁰⁵⁾.



(PDEAEMA)

1-14-2- Biomedical applications :

The applications of hydrogels in biomedical fields are diverse ranging from diagnostic device⁽²⁰⁶⁾ to artificial muscle⁽²⁰⁷⁾. Methylulose hydrogel has been used to deliver allergens in skin testing when test allergens are delivered in the hydrogel vehicle, less skin irritation was observed⁽²⁰⁸⁾. The hydrogel layer not only provide smooth, slippery surface, but also it can prevent bacterial colonization on the surface⁽²⁰⁹⁾.

1-14-3- **Applications in Biotechnology**

Hydrogels have been used as reactive matrix membranes in sensors . Hydrogels possess many advantageous properties , such as rapid and selective diffusion of the analyte . The ability of the smart hydrogels in solutions to reversible swelling and shrinkage with small changes in the environmental condition can be used to prepare purification devices (111) . Smart hydrogels , especially thermo and pH- sensitive hydrogels , have used to concentrate dilute aqueous solution of macromolecular solutes including proteins and enzymes , with no adverse effect on the activity of the enzyme (111) .

1-14-4- **Hydrogel Polymers as Soil Stabilisers**

The need for improving the physical properties of soils led to the development of water – Soluble and hydrogel polymers as soil conditioners (112) .

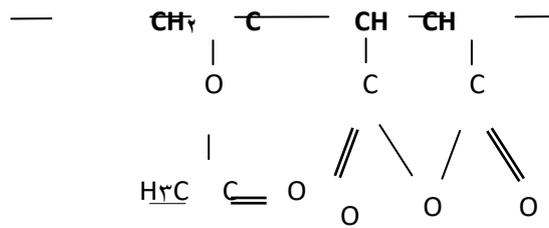
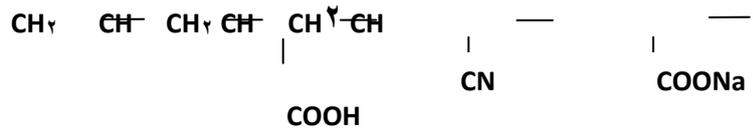
The structure of soil and its related porosity is a major factor with regard to plant growth , erosion and microbial activity . Various naturally occurring materials and agents can stabilise the soil (113, 114) . In most soils a large proportion of the organic material reacts with inorganic colloids to form the clay organic complex (115) .

Much work has been carried out with synthetic organic Polymers , both in attempts to elucidate the interaction between organic materials and inorganic colloids and to evaluate their potential as soil stabilising agent or conditioners . The two materials initially introduced were vinylacetate – maleic anhydride copolymer (VAMA) .

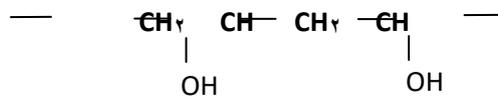
And hydrolysed poly (Acrylonitrile) (HPAN) . The following structures represent some polymers commonly used as soil conditioners (116) .

Hydrolysed poly (acrylonitrile)

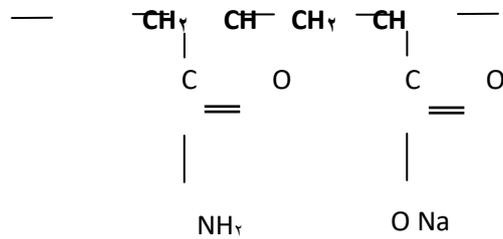
HPAN



Vinylacetate - | Maleic anhydride copolymer (VAMA)

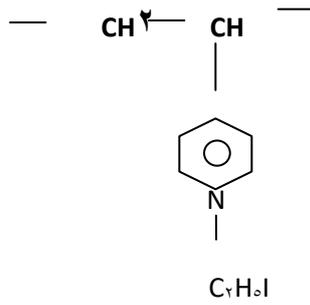


Poly (vinyl alcohol) PVA



Poly (acrylamide)

Pam (ionic)



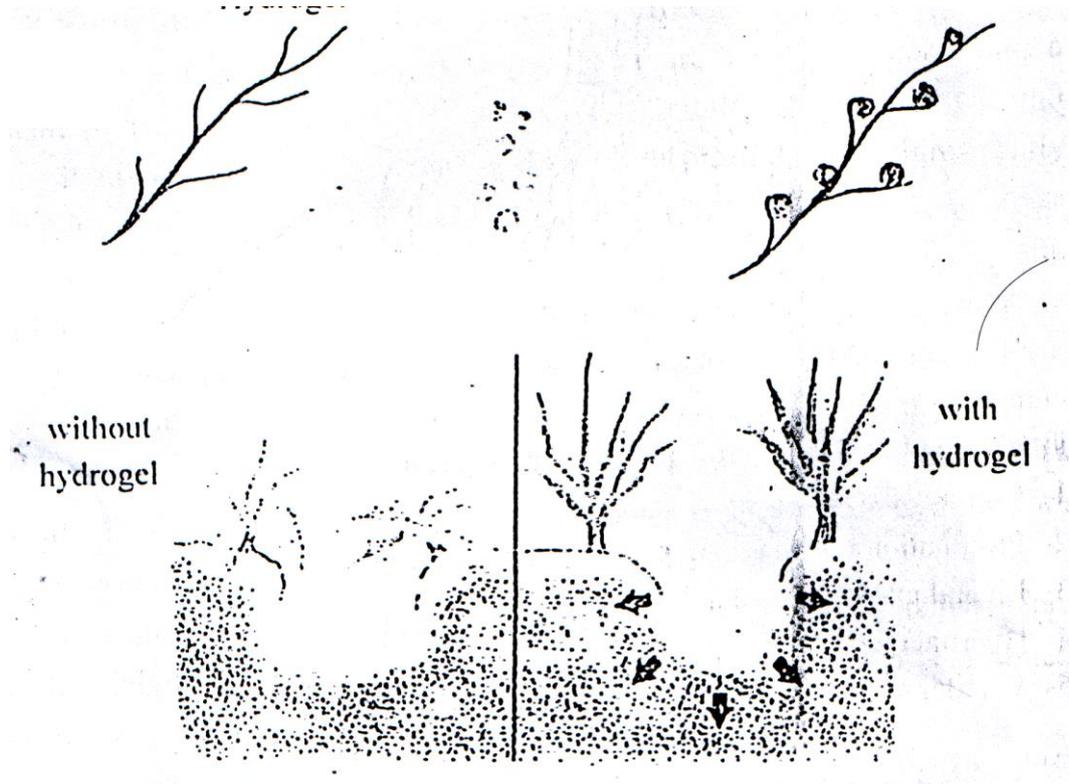
Poly (ϵ -vinyl-N-ethyl peridinium-N-ethylidide) PVPI



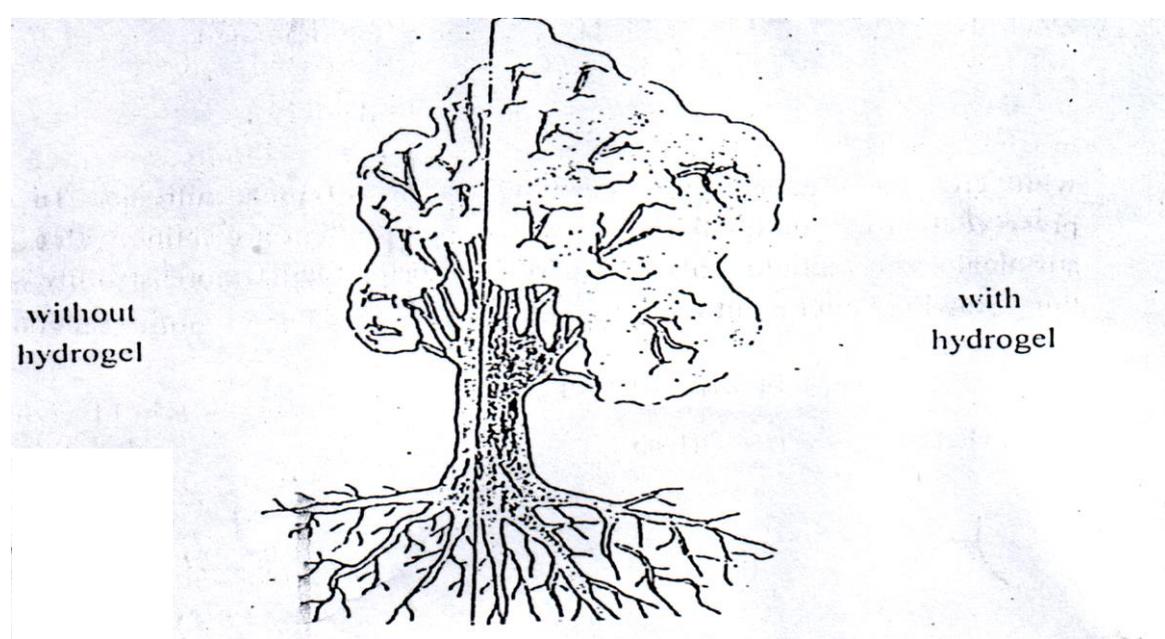
Poly (ethyleneglycol) PEG

Many of polymers evaluated as soil stabilisers are anionic poly electrolytes , e.g. VAMA and HPAN . Some cationic and uncharged polymers are also used but to less extent⁽¹¹⁶⁾ .

Intensive irrigation is the source of seviere damage to soils such as crosion , crust –formation and soil hardening . then naturally , water or wind erosions gradually strip uncovered soils of their nutrients to preserve their natural components and to maintain their protection with a sustainable vegetation , polymers give the surface soils more stability , Thus allowing better plant growth⁽¹¹⁷⁾ .



The hydrogel polymers that absorb and retain large quantities of water and nutrients when dipped into the soil. It optimizes plant growth with minimal losses of water and nutrients through leaching and evaporation. Water and nutrients are stored in the root zone for an optimal uptake by the plant⁽²¹⁾.



Polymers are strongly adsorbed by clay materials . The specific mechanism involved in this interaction depends mainly on the chemical constitution of polymer and the nature of the adsorbent surface . The interaction between organic polymers and clay are (198,199) :

- 1- Cationic exchange .
- 2- Protonation of organic material at clay surface .
- 3- Ligand exchange and anion adsorption .
- 4- Hydrogen bonding .
- 5- Vander waals forces .

Some nonionic and anionic polymeric networks with different ionic groups (such as sulfonate and carboxylate) like crosslinked sulfonate poly styrene (200) , Polyacrylamide (201-203) , Poly ethylene oxide (204) , different ionization degree and different crosslinking ratios have been used as soil conditioners (205) . The ability of poly acrylamide hydrogel to increase the water holding capacity of asandy soil was studied (206-208) .

Poly acrylamide is used in furrow irrigation for erosion control and net infiltration improvement (209) . Polyacrylamide is used also to increase infiltration 15% on silt loam (210) and up to 50% on finer texture soils (211) .

The most effective and environmentally safe polyacrylamide are large negatively charged molecules . It has been found that the divalent cations in water , bridges the polyacrylamide and soil , increasing the soil cohesive and strengthening aggregates contacted in the furrow (212) . Soil particles at the furrows soil – water interface are bounded together . The preventing detachment and transport of sediments in run off . On the other hand the soil erodibility is reduced by improved inter – aggregate bonding and by protecting surface roughness (213) .

Aim of the study :

Due to the wide application of conductive polymers , especially conductive polymer sheets . Therefore it was planned to develop a national technology for production of conductive polymers ; polyethylene sheets by using single and multi filler such as carbon black , graphite and Polyacrylamide .

This involve the following :-

- ١- Preparation of new conductive polymers .
- ٢- study the electrical properties of the prepared polymers .
- ٣- study some factors effecting the electrical conductivity of the prepared polymers .
- ٤- study the mechanical properties of the prepared polymers .

The second part of this study involve the preparation of new hydrogel , polyethylene with polyelectrolyte as filler in the presence of many crosslinking agents . Finally study the swelling and deswelling properaties of the polymer gels .

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Experimental Part

٢-١ Chemicals and Instruments

٢-١-١ Chemicals

The chemicals used in this study were supplied by several sources as follows:-

٢-١-١-١ Low Density Polyethylene (LDPE)

LDPE was obtained from the Iraqi state company for petrochemical/Basrah Industries (SCPI) under the trade name SCPILENE-٤٦٣.

Table (٢-١) shows some physical properties of SCPILENE-٤٦٣.

Table(٢- ١) physical properties of SCPILENE- ٤٦٣(٢٣٤)

Density (at room temp.)	٠.٩٢٢ g/cm ^٣
Melt Index	٠.٣٣ g/١٠ min
Tensile Strength at break	MD-٢١ MPa TD-١٩ MPa
Tensile strength at yield	TD-٩ MPa
Elongation at break	MD-٣١٠٪ TD-٥٥٠٪
Resistance to tear	MD-٢.٥ MPa TD-٥.٥ MPa
Kinetic coefficient	٠.٦

٢-١-١-٢ High Density Polyethylene (HDPE)

Under the trade name SCPILEX-٦٢٤ the HDPE used in the present study was obtained by the Iraqi state company for petrochemical industries / Basrah

Table (٢-٢) shows some physical properties of SCPILEX-٦٢٤

Table(٢- ٢) Physical properties of SCPILEX- ٦٢٤ (٢٢٤)

Density (at room temp)	٠.٩٦٤ g/cm ^٣
Melt index	٦ g/١٠ min
Tensile strength at break	٣٠ MPa
Tensile strength at yield	١٨ MPa
Elongation at break	١١٠٪

٢-١-١-٣- Polyvinyl Chloride (PVC)

This polymer was obtained by the Iraqi state company for petrochemical industries (SCPI) under the trade name SCPNYL-٦٠٨.

The properties of SCPNYL-٦٠٨ are shown in table (٢-٣).

Table (٢- ٣) Physical properties of SCPNYL- ٦٠٨ (٢٢٤)

K-value	٥٣.٠-٥٥.٥
Bulk Density	٠.٥٦ g/cm ^٣
Viscosity Number	٦٩-٩٤
Ash as Sulphates wt%	Nil
Volatile w%	٠.٧٥
SCREEN ANALYSIS	
٤٠ mesh retained on wt%	٠ %
٢٠٠ mesh pass	٤٥ %
PLASTIC ABSORPTION	
g DOP /١٠٠ g PVC	١٠٠

The PVC glass transition temperature (T_g) is about 87°C with critical surface energy equal to 39 mJ/m^2 (1990, 1996), figure (2-1) show the microscope photograph for the PVC.

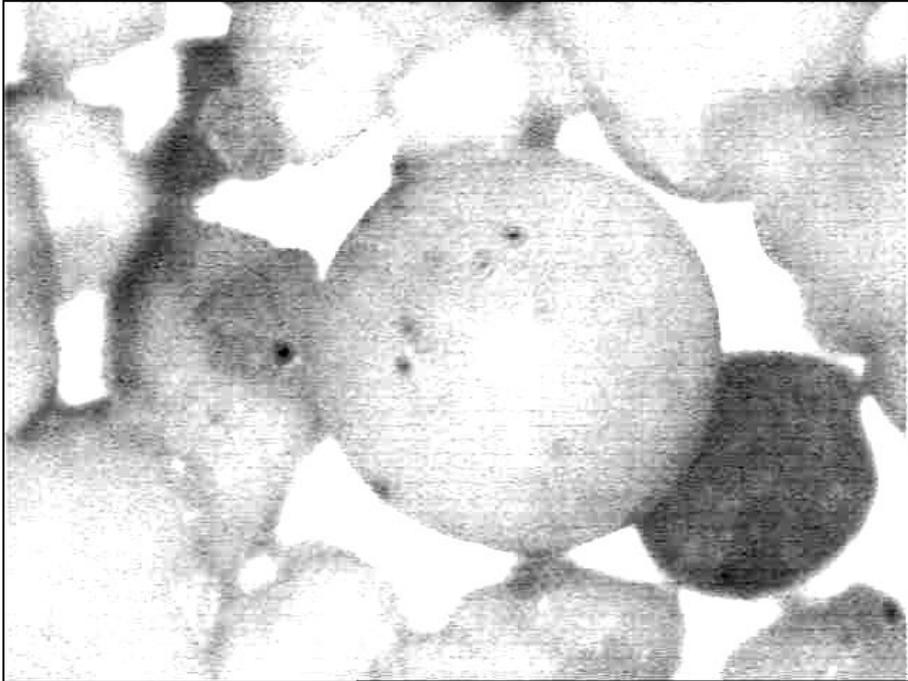


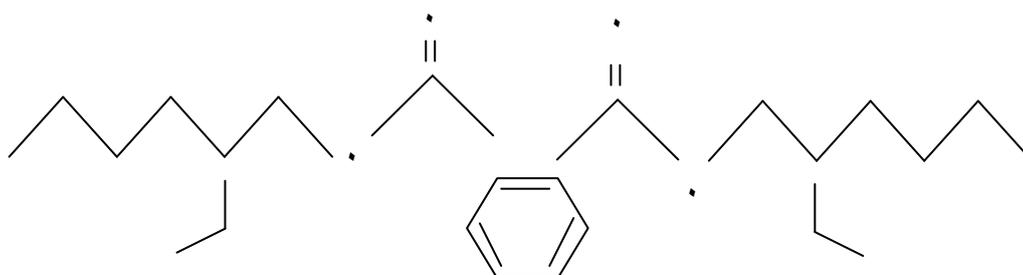
Fig.(2-1) Microscope photograph for the PVC [X40].

2-1-1-4 Di-2-ethylhexylphthalate (DOP) as plasticizer

There are many plasticizers that are used with PVC, among them is the di-2-ethylhexylphthalate commercially called di-octylphthalate (DOP).

DOP combines most of the desirable properties of plasticizer such as minimal interaction with the resin at room temperature, good fusion properties, low volatility, colorless, low cost, and good compatibility. The boiling point of DOP is 231 °C (447).

The chemical structure of DOP is :



The DOP plasticizer, used in this study was supplied by the national company for chemical and plastics industries (Iraqi-Baghdad) with the properties listed in table(٢-٤).

Table(٢-٤) The properties of DOP^(٢٣٨)

Acid value	٠.٠٥ max
Water cont.	٠.٠٥ max
color	Colorless
Volatility ٢ hours, at ١٣٠ °C	٠.٢% max
Refractive index	١.٤٨٧

Density at 200 °C g/cm ³	0.9830-0.9840
Specific electrical resistance at 20 °C	Approx. 2x10 ⁶ μΩ.cm

2-1-1-5 Carbon Black

There are many types of carbon black, depending on the type of the raw material and the processing technique. Wood, resin, coal, pitch, tar oils and recently polymers were all used as raw materials to produce carbon black⁽²³⁹⁻²⁴¹⁾. Furnace black, gas black and channel black, lamp black, thermal black and recently acetylene black are essential processes used to produce carbon black⁽²⁴²⁾.

The carbon black used in this study was supplied by Degussa Co.

Whose properties are shown in table (2-5).

Table(2-5) properties of carbon black⁽²⁴⁾

Nigrometer index value	64
Tinting strength	0.86
Oil absorption (F-P)	88.0/100g
Volatility	0%
Moisture max	6%
Acetone extract	0.3%
Ash of powder	0.05%
Compact Density	0.13 g/cm ³
PH value	4
Average particle size arith, MgM	128-132 A ^o

N ₂ surface area (to BET method)	32. m ² /g
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figure (2-2) show the microscope photograph for the carbon black powder .

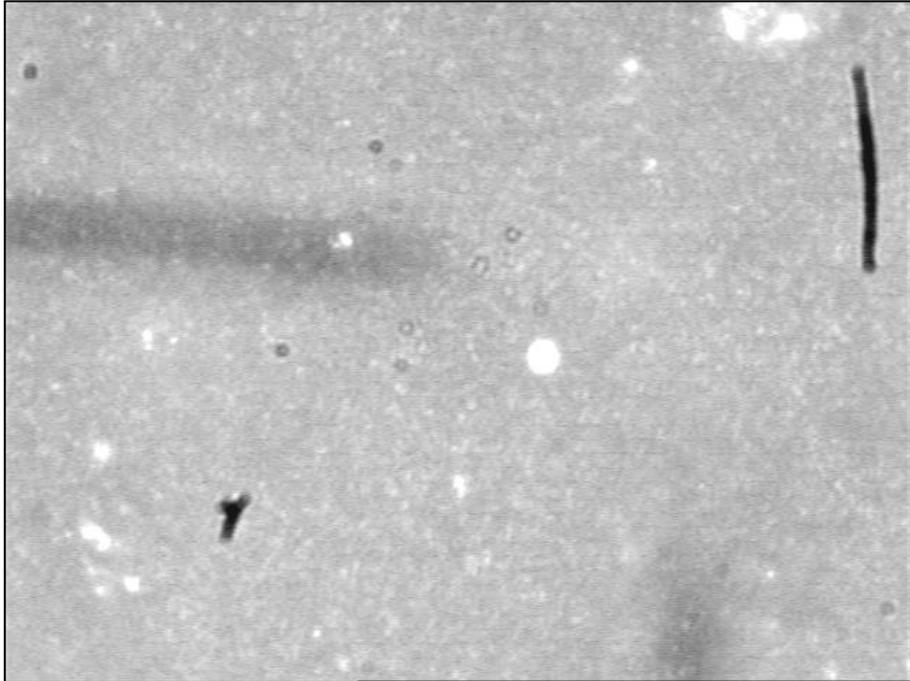


Fig.(2-2) Microscope photograph for the carbon black [X40]

2-1-1-6 Graphite

Petroleum coke is the main raw material used in synthesis of graphite. Coke from refinery is usually been heated to approximately (400-500)°C and contains up to 10% volatile materials.

Chinese synthetic graphite was used in this study which is available from the local markets with the specifications and properties shown in table (2-6). This material has been sieved with 100 μ m sieve to isolate any large particles from the powder.

Table 2-6 specifications and properties of synthetic graphite

Ash	< 0.1 wt%
Sulfur	0.02 wt%
Density	2.24 g/cm ³
Thermal Conductivity	0.0 W/m.K
Electrical Resistance	10 ⁻⁶ Ohm-cm
Particle size	Irregular

figure (2-7) show the microscope photograph for the graphite.



Fig.(٧-٣) Microscope photograph for graphite [X٤٠]

٧-١-١-٧- Poly acrylamide

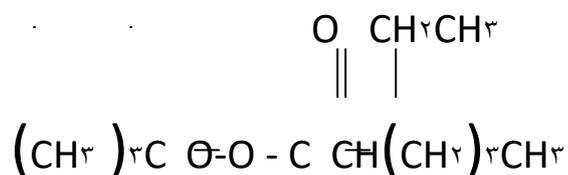
The poly acrylamide used in this project was supplied by Aldrich Co.

٧-١-١-٨- Hexamethlene tetramine (HMTA)(Hexamine) ٩٩%

$(CH_2)_6 N_4$, $M_w = 144$ was supplied by Al- KaKaa Gen. Co.(Iraq).

٧-١-١-٩- t-Butyl peroxy-ethyl hexanoate (C_{17})

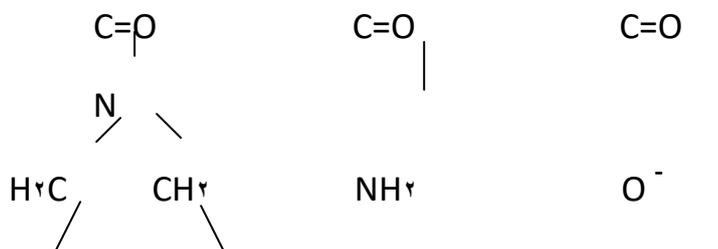
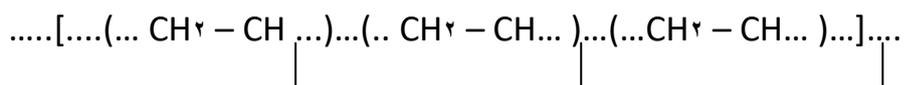
The (C_{17}) used in this project was supplied by pergan G.m.b.H Co.



C_{17}

٧-١-١-١٠- Polyelectrolyte : this Resin using in special of stable

pools for water product (R . O) .



ξ- Cutter instruments-type Dipuach outomatic hollow, supplied by Ceast Co. Italy.

ο-Microsmeter-type LIS starett Co. LTD.

ϖ- Stress-strain properties instruments, using instrone testing instruments model 1193, the Iraqi state company for petrochemical industries (SCPI) presents , with following specifications:-

-Cross sheet speed (0-0.1 mm/min)

-Chart speed (1-1000 mm/min)

-Tension load (Cell 1000 N)

-Temperture of measurment

ϗ- Notching instruments, using instrument TMI notching cutter model 10-1, supplied by TMI organization U.S.A., (SCPI) presents .

λ- Hardness tester instruments, using shore instrument type - D & A, supplied by MIFG.Co.INC., U.S.A. , (SCPI) presents, with following specifications:-

a- Inner diameter= 0.1 ± 0.01 mm.

b- Load maximum = 0.1 ton.

Ϙ- Impact strength instrument, instrument model universal pondulums (60461000), , (SCPI) presents, supplied by Ceast.Co.Italy.

ϙ- FTIR Spectra , Type Shemadzu (FTIR 4400S) Japan .

Ϛ- Conductivity measurements instrument:-

The conductivity measurements were carried at using conductivity bridge ; wyne kerr ; Auto balance precision bridge, type (B331 MKII); shown in

Fig.(٢-٤) . An (AC) electrical used for conductivity measurement of frequency, (1097.00 ± 0.0 HZ). Detectors, one of them for capacitor specific and the another for conductivity as well as variable capacitor for capacity balance in cell. At the start, the instrument was equilibrated using box resistance.

The equilibrium instrument using the above mentioned resistance box. Instrument precision is (± 0.01 %), for range ($10^{-1} - 10^6$ ohm)^(٢٣٧).

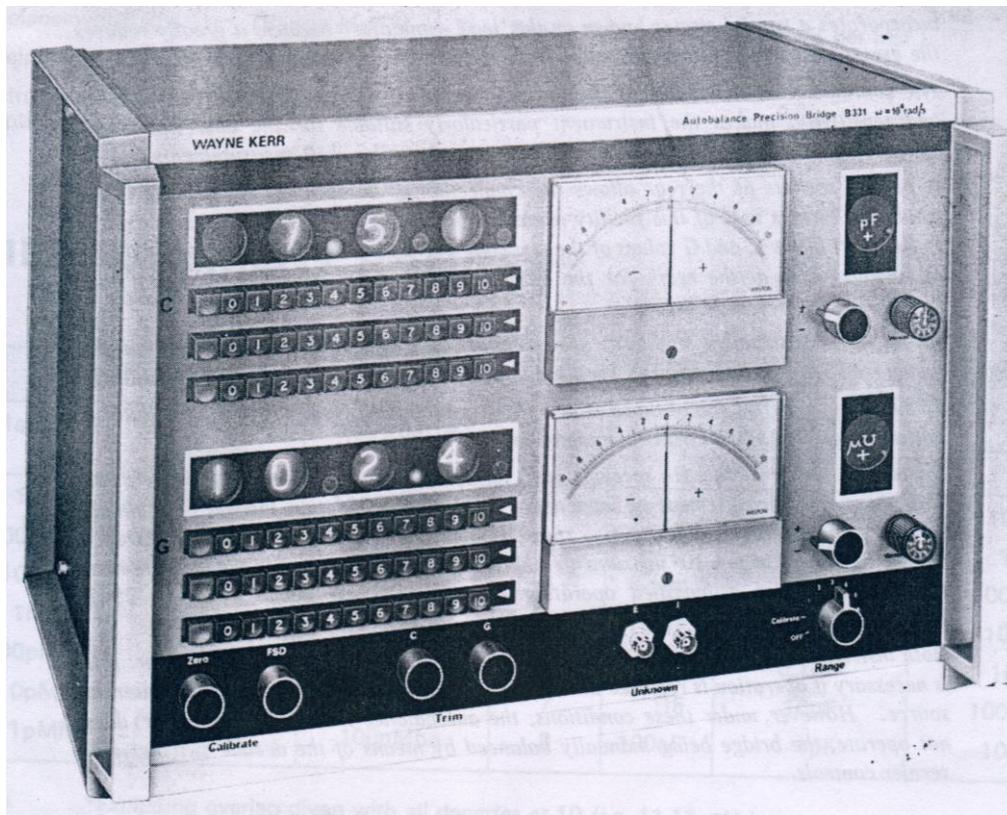


Fig.(۲-۴)Auto balance precision bridge, type (B۳۳۱ MKII) instrument

۲-۲- Samples preparation :

۲-۲-۱- Preparation of the new(PVC) polymer composites

Polyvinylchloride (PVC) mixed with ۴۰% DOP then different percentage of carbon black (C) and graphite (G) was added .The prepared sample and quantities are listed in table (۲-۷).

The obtained polymer samples were placed in the mold and heated to 100 ± 0 °C , kept at this temperature under (۰) ton pressure for ۱۰-۲۰ min. , then the pressure was elevated to (۷-۸) ton and the temperature was increased to 100 ± 0 °C. The system was kept under these conditions for an other (۱۰ min), Finally different sheets in thickness was obtained and removed from the mold system^(۲۴۳,۲۴۴).

Table (۲- ۷) the PVC composite of ۴۰% DOP with different wt% fillers(C+G)

Sample	Polymer wt%	DOP wt% for PVC	C wt% for PVC	G wt% for PVC	Label
۱	PVC	۴۰	۰	۰	PDC
۲	PVC	۴۰	۳۷.۰	۱۲.۰	PDC _r G _۱

٣	PVC	٤٠	٢٥	٢٥	PDCG
٤	PVC	٤٠	١٢.٥	٣٧.٥	PDC _١ G _٢
٥	PVC	٤٠	٠	٥٠	PDG

٢-٢-٢- Preparation of Polyethylene Sheets .

The samples were molded using compression molding technique by using a set consisted of a hot plate and hydraulic press^(٢٤٣,٢٤٤).

For the polyethylene composite samples, the temperature raised to ١١٠ °C for the LDPE and ١٥٥ °C for the HDPE with pressure about ٦-٧ tons for both. The mold temperature was measured by a thermocouple fitted into the mold. The mold was kept at ١١٠ °C for about ١٥-٢٥ min. and then raise to ١٣٠ °C for the LDPE and ١٧٠ °C for the HDPE and kept at for about ١٠ min. The mold was cooled and the formed sheets were removed from the mold.

٢-٢-٣- Preparation of the conductive polyethylene

The formed sheets of polyethylene with different thickness from (١-٢)mm. ,as well as the formed sheets of (PVC) to a thickness from ٠.١ to ٠.٥ mm. were used to prepare sample . The (PVC) sheets put each side for

sandwiching polyethylene sheets according to the compression molding for sandwich method^(٢٤٥). The conditions for the prepared samples were heated to 100 ± 0 °C under (٥) ton pressure for ١٥-٢٥ min., then the pressure elevated to (٧-٨) ton and the temperature was raised to

100 ± 0 °C. The system was kept under these conditions for another (١٠ min) , after that cooled for mold system^(٢٤٣,٢٤٤). The quantities of the components are listed in tables (٢-٨ to ٢-١٧).

Table (٢-٨) the LDPE with different percentage of PDC

Sample No	LDPE Wt(gm)	PDC Wt(gm)	Label
١	٢	٠.٠	LDPE
٢	١.٨	٠.٢	L _{١,٨} PDC
٣	١.٦	٠.٤	L _{١,٦} PDC
٤	١.٤	٠.٦	L _{١,٤} PDC

٥	١.٢	٠.٨	L _{١.٢} PDC
٦	١.٠	١.٠	LPDC

Table (٢- ٩) the LDPE with different percentage of PDC_rG_١

Sample No	LDPE Wt(gm)	PDC _r G _١ Wt(gm)	Label
١	٢	٠.٠	LDPE
٢	١.٨	٠.٢	L _{١.٨} PDC _r G _١
٣	١.٦	٠.٤	L _{١.٦} PDC _r G _١
٤	١.٤	٠.٦	L _{١.٤} PDC _r G _١
٥	١.٢	٠.٨	L _{١.٢} PDC _r G _١
٦	١.٠	١.٠	LPDC _r G _١

Table (٢- ١٠) the LDPE with different percentage of PDCG

Sample No	LDPE Wt(gm)	PDCG Wt(gm)	Label
۱	۲	۰.۰	LDPE
۲	۱.۸	۰.۲	L _{۱.۸} PDCG
۳	۱.۶	۰.۴	L _{۱.۶} PDCG
۴	۱.۴	۰.۶	L _{۱.۴} PDCG
۵	۱.۲	۰.۸	L _{۱.۲} PDCG
۶	۱.۰	۱.۰	LPDCG

Table (۲-۱۱) the LDPE with different percentage of PDC_۱G_۲

Sample No	LDPE Wt(gm)	PDC _۱ G _۲ Wt(gm)	Label
۱	۲	۰.۰	LDPE
۲	۱.۸	۰.۲	L _{۱.۸} PDC _۱ G _۲
۳	۱.۶	۰.۴	L _{۱.۶} PDC _۱ G _۲
۴	۱.۴	۰.۶	L _{۱.۴} PDC _۱ G _۲
۵	۱.۲	۰.۸	L _{۱.۲} PDC _۱ G _۲
۶	۱.۰	۱.۰	LPDC _۱ G _۲

Table (٢- ١٢) the LDPE with different percentage of PDG

Sample No	LDPE Wt(gm)	PDG Wt(gm)	Label
١	٢	٠.٠	LDPE
٢	١.٨	٠.٢	L _{١.٨} PDG
٣	١.٦	٠.٤	L _{١.٦} PDG
٤	١.٤	٠.٦	L _{١.٤} PDG
٥	١.٢	٠.٨	L _{١.٢} PDG
٦	١.٠	١.٠	LPDG

Table (٢- ١٣) the HDPE with different percentage of PDCG

Sample No	HDPE Wt(gm)	PDCG Wt(gm)	Label
١	٢	٠.٠	HDPE
٢	١.٨	٠.٢	H _{١.٨} PDCG
٣	١.٦	٠.٤	H _{١.٦} PDCG
٤	١.٤	٠.٦	H _{١.٤} PDCG
٥	١.٢	٠.٨	H _{١.٢} PDCG
٦	١.٠	١.٠	HPDCG

٢-٢-٤- Preparation of the new polymer (LDPE with Polyacrylamide(PAM)) crosslinked by hexamine(HM)

The formed sheets of LDPE was crosslinked with the PAM by hexamine (HM), with the compression molding for sandwich method^(٢٦٣), the PAM powder put each side for sandwiching LDPE sheets and adding (HM) each side. The molding heated to 100 ± 0 °C and kept at this temperature under (0) ton pressure for 10-20 min. The pressure was elevated to (٧-٨) ton and the temperature was increased to 120 ± 0 °C, the system was kept under these conditions for an other (10 min), after this the system cooled^(٢٤٣,٢٤٤). The polymer obtained by using the quantities listed in table (٢-١٤).

Table (٢- ١٤) the LDPE with(1- ٣ %wt PAM) crosslinked by different percentage %wt of (HM)

%wt PAM	HM (%wt)					
	٠.٠%	٢.٥%	٥%	٧.٥%	١٠%	١٢.٥%
١%	LAM _١	LAM _١ HM _{٢.٥}	LAM _١ HM _٥	LAM _١ HM _{٧.٥}	LAM _١ HM _{١٠}	LAM _١ HM _{١٢.٥}
٢%	LAM _٢	LAM _٢ HM _{٢.٥}	LAM _٢ HM _٥	LAM _٢ HM _{٧.٥}	LAM _٢ HM _{١٠}	LAM _٢ HM _{١٢.٥}
٣%	LAM _٣	LAM _٣ HM _{٢.٥}	LAM _٣ HM _٥	LAM _٣ HM _{٧.٥}	LAM _٣ HM _{١٠}	LAM _٣ HM _{١٢.٥}

2-2-5- Preparation of the new polymer (LDPE with polyacrylamide-PAM) crosslinking by Gluteraldehyde (Ga)

The compression molding for sandwich method⁽²⁶²⁾, the PAM powder put each side for sandwiching LDPE sheets and adding (Ga) percentage each side. The conditions for molding heated to 100 ± 0 °C and kept at this temperature under (0) ton pressure for 10-20 min. The pressure was elevated to (5-8) ton and the temperature was increased to 120 ± 0 °C, for another (10 min), after that left to cool^(243,244), the obtained polymer prepared using the quantities listed in table (2-10).

Table (2-10) the LDPE with (%wt) PAM crosslinked by different percentage of (%wt) Ga

PAM (%wt)

Ga(%wt)	0%	1%	2%	3%	4%	5%
0%	LGa ₀	LAM ₁ Ga ₀	LAM ₂ Ga ₀	LAM ₃ Ga ₀	LAM ₄ Ga ₀	LAM ₅ Ga ₀
1.5%	LGa _{1.5}	LAM ₁ Ga _{1.5}	LAM ₂ Ga _{1.5}	LAM ₃ Ga _{1.5}	LAM ₄ Ga _{1.5}	LAM ₅ Ga _{1.5}
3%	LGa ₃	LAM ₁ Ga ₃	LAM ₂ Ga ₃	LAM ₃ Ga ₃	LAM ₄ Ga ₃	LAM ₅ Ga ₃

2-2-6- Preparation of the new polymer (LDPE) with (PAM) crosslinking by C_{1v}

The compression molding for sandwich method⁽²²²⁾, The PAM powder put each side for adding it (C_{1v}) a crosslinking agent percentage each side. The conditions for molding heated to 100 ± 5 °C and kept at this temperature under (5) ton pressure for 10-20 min. The pressure was elevated to (7-8) ton and the temperature was increased to 120 ± 5 °C, the

other (10 min), after this cooled for system^(223,224), The obtained polymer prepared using the quantities listed in table (2-16).

Table (٢- ١٦) the LDPE with (% wt) (PAM) crosslinked by different (% wt)

$C_{١٧}$

$C_{١٧}(\%wt)$	PAM (% wt)					
	٠%	١%	٢%	٣%	٤%	٥%
٥%	LC _{١٧,٥}	LAM _١ C _{١٧,٥}	LAM _٢ C _{١٧,٥}	LAM _٣ C _{١٧,٥}	LAM _٤ C _{١٧,٥}	LAM _٥ C _{١٧,٥}
٧,٥%	LC _{١٧,٧,٥}	LAM _١ C _{١٧,٧,٥}	LAM _٢ C _{١٧,٧,٥}	LAM _٣ C _{١٧,٧,٥}	LAM _٤ C _{١٧,٧,٥}	LAM _٥ C _{١٧,٧,٥}
١٠%	LC _{١٧,١٠}	LAM _١ C _{١٧,١٠}	LAM _٢ C _{١٧,١٠}	LAM _٣ C _{١٧,١٠}	LAM _٤ C _{١٧,١٠}	LAM _٥ C _{١٧,١٠}

٢-٢-٧- Preparation of the new polymer (LDPE) with

polyelectrolyte (PE) crosslinked by (HM , Ga , $C_{١٧}$)

The compression molding for sandwich method^(٢٤٥), The polyelectrolyte (PE) powder put each side for adding it (HM) a crosslinking agent (٥% w/w) each side. The conditions for molding heated to ١٠٠ ± ٥ °C and kept at this temperature under (٥) ton pressure for ١٥-٢٥ min. The pressure was elevated to (٧-٨) ton and the temperature was increased to ١٢٠ ± ٥ °C, the other (١٠ min), after this cooled for system^(٢٦٠,٢٦١). The above operations were repeated with (Ga & $C_{١٧}$) a crosslinking agent (٥% w/w) each side. The obtained polymer prepared using the quantities listed in table (٢-١٧).

Table (٢- ١٧) the LDPE with (% wt) (PE) crosslinked by different

agent(HM , Ga , $C_{١٧}$) (٥% w / w)

PE (% wt)					
(% wt)	1%	2%	3%	4%	5%
0% HM	LPE ₁ HM	LPE ₂ HM	LPE ₃ HM	LPE ₄ HM	LPE ₅ HM
0% Ga	LPE ₁ Ga	LPE ₂ Ga	LPE ₃ Ga	LPE ₄ Ga	LPE ₅ Ga
0% C _{1V}	LPE ₁ C _{1V}	LPE ₂ C _{1V}	LPE ₃ C _{1V}	LPE ₄ C _{1V}	LPE ₅ C _{1V}

2-3- Mechanical Properties Measurements

The mechanical properties may be considered as the most important properties of materials for most applications, generally dealing with materials designer require information about their mechanical behaviour and how this behaviour can be measured by mechanical testing e.g. tensile strength, hardness, impact strength,....etc^(*).

2-3-1- The stress- strain Behaviour Measurements

The dumbbell shaped cutting machine, the specimens were cut from the leathery preheated sample sheets.

The specimens were numbered at both ends and their dimensions were measured accurately at several different parts of the specimens by micrometer, in order to average the obtained dimensions, mainly the width and thickness.

The sets of samples consisting 10 samples were tested from each category, schematic diagrams with dimensions for the tested specimens are presented in fig. (1-5).

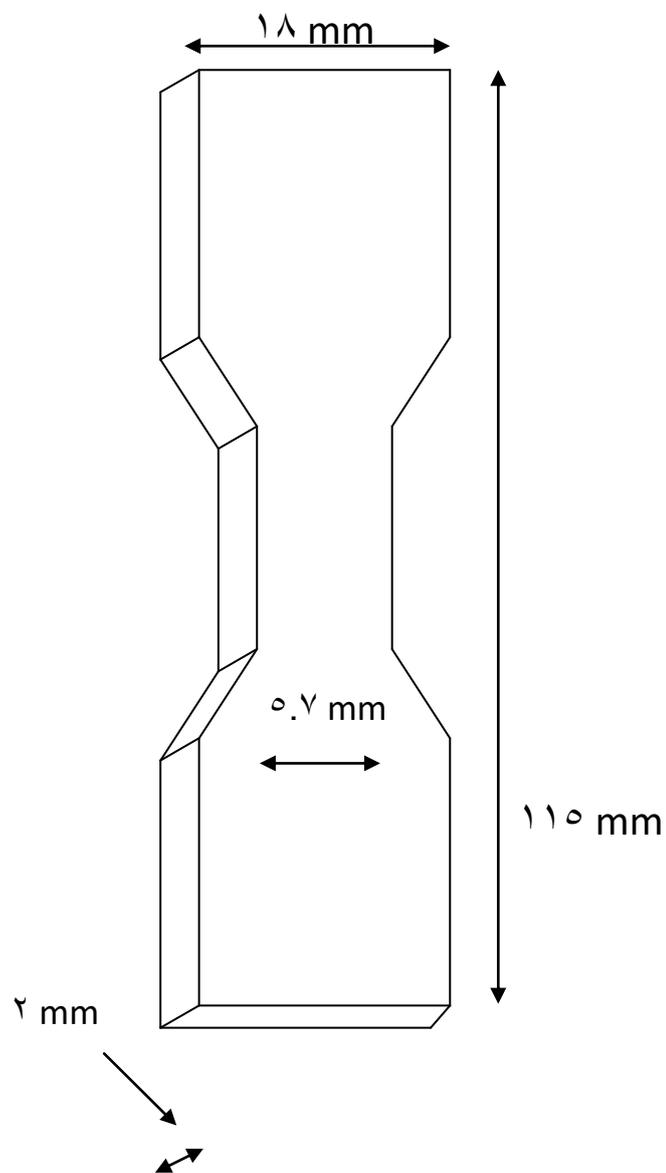


Fig (2-0) Schematic diagram for tensile testing dumbbell shaped specimen.

All the measurements for tensile testing evaluation were carried out according to ASTM D 638 (2003).

The specimens were subjected to constant stress at constant rate of strain, cross sheet speed 0.5 mm/min, the load-elongation curves were recorded for each test on chart recorder with speed 10 mm/min.

The load-elongation curves were recorded for each sample and the obtained load-elongation curves were analyzed for all samples. Thus each of the dumbbell shaped specimens was numbered from both ends and clamped in jaws of the testing machine, the elongation was measured over a portion of the narrowed section from the sample (termed the a gage length).

2-3-2 Impact Strength

2-3-2-1 Preparation of the Specimens

The sample sheets prepared are the parallel strips cut from the preheated sheets the parallel strips were cut small strips convenient to impact measurements, the dimensions, of the small strips were chosen to be according to ASTM D²⁰⁶ having dimensions, length (60.0 mm), width (12.7 mm) and thickness (3 mm), diagram for representative sample is shown in fig. (2-6).

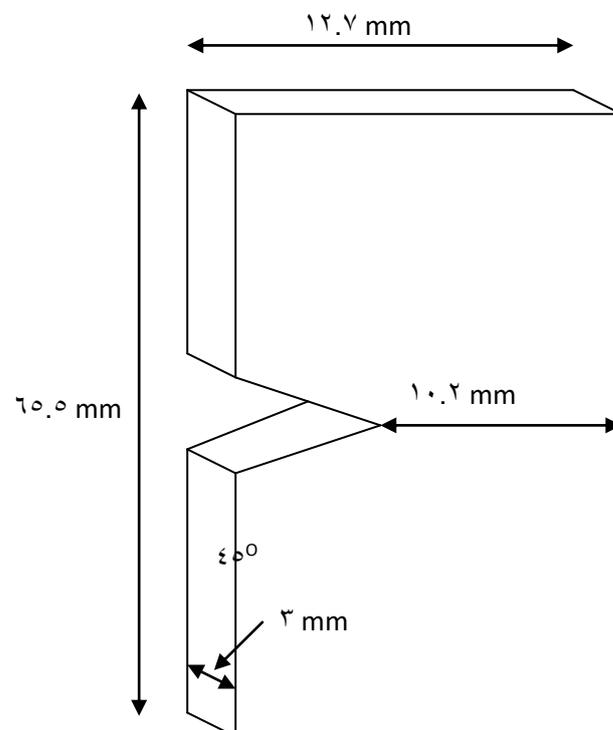


Fig (٢-٦) IZOD impact testing specimen

The sample were notched via making V-shape notch with angle (45°) and depth (٢.٥ mm), samples were prepared from each of the prepared samples, the specimens were treated and preconditioned adopting the same sequence at various sages similarly to tensile strength samples as already, for the tensile testing specimens in order to delete the micro crazes and rough surface by grinding techniques. The required dimensions of the samples were measured accurately by micrometer.

٢-٣-٢-٢ Measurements of the Impact Strength

All the specimen were tested by IZOD impact tester. Each specimen was placed vertically and facing the hammer at nearly standard testing conditions. The impact strength was calculated by equation (١-٦), fig (٢-٧) shows the impact strength testing diagram.

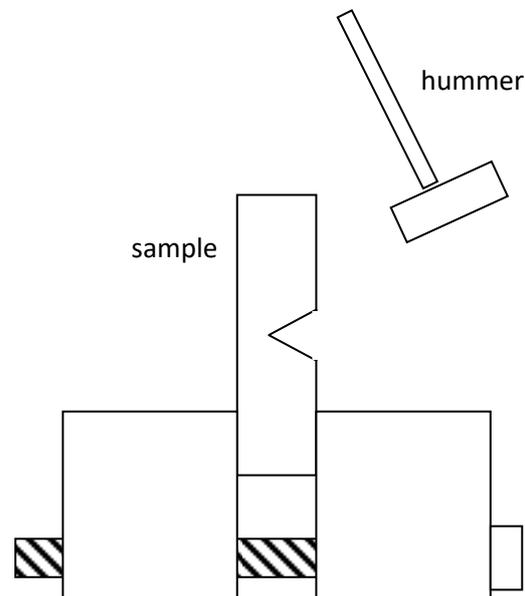


Fig.(٢-٧) IZOD impact testing

۲-۳-۳- Hardness tests

۲-۳-۳-۱ Hardness measurements

The hardness characteristics of the prepared samples was measured using shore hardness tester type-D&A.

Fig (۲-۸) shows a representative hardness of specimen.

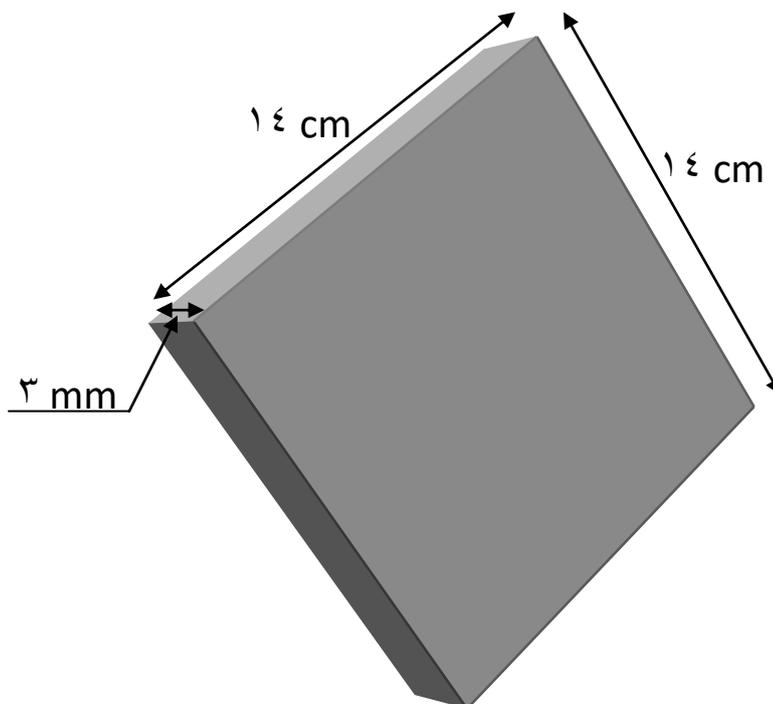


Fig (۲-۸) Hardness testing specimen

The measurements for hardness testing evaluation were carried out according to ASTM-D2240.

In shore-D, the specimen prepared (3 mm) thickness put in instruments and the indenter down to for specimen at load (10 N) for 10 sec. The hardness was measured at several different parts of the samples, the obtained values were averaged.

In shore -A, specimen prepared (3 mm) thickness put in instruments and the load (5 N) was down for one sec. The hardness was measured at several different parts of the samples, the obtained values were averaged.

2-4- Electrical Properties of Polymers

2-4-1 The conductivity measurements for the solid samples:

The conductivity measurements for the new polymer (LDPE), (2x2) cm and 0.2 mm thickness. The conductivity (G)(ohm) and capacity (C)(F/m) measured for the samples, for different temperature (20-30) °C and different time (0-10)min for any temperature .

2.5- Swelling Behavior of the New Hydrogels

2.5.1- Swelling Studies as a Function of Time :

The dry samples were allowed to hydrate in the presence of excess amount of distilled water at (30±0) °C. The weight of the hydrated samples was measured at different time intervals using (Digital Balance Oertling JC 12) by removing the gels from water and blotting them to remove the superficial water and weighting in a closed weighting bottle. Some hydrogels swelled to the extent that they became too fragile to handle. These were placed in a weighting boat. The weighting boat containing the hydrogels was immersed in distilled water for swelling. The weighting boat was taken out to drain the free water from the sieve. The excess of water underneath the sieve was removed

by towel paper. Then the weight of the swollen hydrogels was measured by subtracting the boat weight from the total weight.

The swelling ratio (Q) is defined as :-

$$Q = (w_s - w_d) / w_d$$

Where w_s is the weight of the swollen hydrogel and w_d is the weight of the dried hydrogels. Also (Q) can be defined as water up take (g water/g dry gel) ^(2.47-2.50).

2.5.2 Deswelling Studies:-

The swollen hydrogels were dried for 24 hours under blowing of warm air (30 ± 5) °C.

3.1- Electrical properties of polymers

The electrical properties of polymers were distinguish for many manifestly not normal for most inorganic semiconductors.

Such as ; Firstly , It's values are very low were do not measured by (Hall effect) (less than 10^{-1} cm²/V.sec). Secondly; the electrical motive force (EMF)

α

α

and the thermal factor () are constants and increased with temperature, i.e. (log) increased linearly with heating . This happens for all semiconductors. Thirdly ; for electrons of heterogeneous compounds when conductor layers separated by veils isolators.^(٣٤١) Therefore there is many theories to explain polymer conductivity behavior^(٣٥١) .

٣-١-١- Electrical conductivity

The electrical conductivity of polymer defined as the charge quantity throughout passing time unit in unit area , for conductor electrical field unit. The electrical conductivity of polymer(x) depends on found free ions which do not chemically connected with large molecular and this molecule do not involve in electrical charges transport process , therefore the polymers conductivity depends on interference founding in large degree for that low molecular weight for ions reference .

When the chemical structure of polymer is the limited effect for ions movement , makes the conductivity of polymer in the glass state in the range (١٠^{-١٣} - ١٠^{-١٩}) ohm^{-١} . cm^{-١} , the conductivity value increase with temperature increase , equation (٣ - ١) become :

$$X = A e^{-\Delta u/RT} \dots\dots\dots (٣-١)$$

A : is constant (A ∝ 1/T)

R : gas constant .

Δu : activation energy .

When the temperature is higher than glass transition temperature (Tg) , the ions movement will increased , resulted to higher proportion movement of polymer chain ends which lead to higher conductivity ⁽³⁰⁾ .

3-1-2- Permittivity

The Permittivity or dielectric constant for polymers (ϵ) depends on the capacity of electrical capacitor capacity in absolute space in the outer electrical field frequency .

3-1-3- The measurements of electrical conductivity of the prepared polymers

Electrical conductivity measurement of prepared polymers conductivity (G) , capacity (C) and permittivity or dielectric constant (ϵ) of the prepared polymer were measured at different temperature (27 – 110 °C) and different time (0 – 180 min.) . The dielectric constant (ϵ) was calculated by the following equations .

$$\epsilon = \frac{C}{\dots\dots\dots(3-2)}$$

C₀

Where the C : Capacity of polymer

C₀ : absolute capacity which is equal to

a

$$C_0 = \epsilon_0 \frac{a}{l} \dots\dots\dots (\text{3-3})$$

Where the (ϵ_0) represented of air permittivity (8.85×10^{-12}) f/m, when (a) represents one knit area , (l) represents distance between two parallel knits

$$a = r^2 \times \pi \dots\dots\dots (\text{3-4})$$

Where r : radius of polymer sample

The resistivity (ρ) of polymer defined is inverse of solution conductivity (K), in relationship⁽³⁻⁵⁾ :

$$\rho = 1/K \dots\dots\dots (\text{3-5})$$

Fig.(3-1) shows the resistivity(ρ)of prepared polymer (LPDC) [Table (3-1) page 68] with the time at different temperature .Its clearly noticed that the resistivity(ρ) value decreases with increasing temperature , its value were [4.01×10^8 , 6.20×10^7 , 2.61×10^6 , 1.30×10^5 , 4.61×10^3 , 4.60×10^2 and 4.76×10^2 ohm.cm] at temperature [$28, 40, 50, 70, 90, 100$ and 110 °C] respectively . The

ρ

resistivity(ρ) value increased with the time up to (10 min.) and then level off at (100°C) . While about same trends were noticed for others temperature i.e. no change (ρ)of with time except at (100°C) where a decreases up to (10 min.)then level off . This is may be due to for annealing or creastilaization on heating of polyethylene in temperature less than melting point (T_m) ($100-100^\circ\text{C}$) .

The behavior polymer(**LPDC**) permittivity (ϵ) with the time in different temperature is shown in Fig.($3-2$). Where the permittivity (ϵ) remain constant with time up to (10 min.) and then remain constant except at (100°C) a fluctuation behavior was noticed which could be due to for annealing or creastilaization on heating of polyethylene in temperature less than melting point (T_m) ($100-100^\circ\text{C}$) .

Fig.($3-3$) shows the resistivity(ρ) of prepared polymer (**L₁:PDC**) [Table ($2-8$) page 18] with the time at different temperature .Its clearly noticed that the resistivity(ρ) value decreases with increasing temperature , its value were [1.0×10^4 , 1.44×10^4 , 1.0×10^4 , 3.0×10^4 , 0.2×10^4 , 1.1×10^4 and 1.66×10^4 ohm.cm] at temperature [$100, 100, 100, 100, 100, 100$ and 100°C] respectively . The resistivity(ρ) value increased with the time up to (10 min.) and then level off at (100°C) . While about same trends were noticed for others temperature i.e. no change (ρ)of with time except at (100°C) where a ρ decreases up to (10 min.)then level off . This is may be due to for annealing or cross linking reactions between polyethylene and other compound (100) .

The behavior polymer(L_{1.4}PDC) permittivity (ϵ) with the time in different temperature is shown in Fig.(3-5). Where the permittivity (ϵ) remain constant with time up to (10 min.) and then remain constant except at (20 °C) a fluctuation behavior was noticed which could be due to for annealing or cross linking reactions between polyethylene and other compound (200) .

Fig.(3-6) shows the resistivity(ρ) of prepared polymer (L_{1.4}PDC) [Table (3-4) page 14] with the time at different temperature .Its clearly noticed that the resistivity() value decreases with increasing temperature , its value were [1.17×10^8 , 9.09×10^7 , 9.02×10^7 , 1.4×10^8 , 9.48×10^8 , 6.94×10^8 and 6.08×10^8 ohm.cm] at temperature [23, 25, 27, 29, 31 and 33 °C] respectively . The resistivity() value increased with the time up to (10 min.) and then level off at (20 °C) . While about same trends were noticed for others temperature i.e. no change ()of with time except at (23, 25 °C) where a ρ decreases up to (10 min.)then level off . This is may be due to for happens for molecular orientation type ,annealing or creastilaization on heating of polyethylene in temperature less than melting point (Tm) (202-204) .

The behavior polymer(L_{1.4}PDC) permittivity (ϵ) with the time in different temperature is shown in Fig.(3-7). Where the permittivity (ϵ) remain constant with time up to (10 min.) and then remain constant except at (23 °C) a fluctuation behavior was noticed which could be due to for happens for molecular orientation type ,annealing or creastilaization on heating of polyethylene in temperature less than melting point (Tm) (202-204) .

When the conductivity of solid (un plasticized) PVC is in the order of $(1 \cdot 10^{-14} \text{ s/cm})$ while the conductivity of the DOP plasticizer is about $(\rho \times 10^{-12} \text{ s/cm})$, when the DOP level increased the composites conductivity increased independent on the filler conductivity like this carbon black is in the order of $(1 \cdot 10^4 \text{ s/cm})$. Fig. (3-7) show the log resistivity ($\log \rho$) with the temperature ($^{\circ}\text{C}$) for to polymers prepared (LPDC ,L1.4PDC, L1.8PDC) we notice the temperature increase the ($\log \rho$) is decrease this meaning the conductivity is increase for three polymers .In polymer (LPDC) when the ($\log \rho$) is $(\xi.\xi\cdot)$ in $(\rho\cdot^{\circ}\text{C})$ is the (ρ) $(\gamma.\rho\gamma \times 10^{\xi} \text{ ohm} \cdot \text{cm})$ and after this point is stay constant . In polymer (L1.4PDC) when the ($\log \rho$) is $(\xi.\gamma\gamma\gamma)$ in $(\gamma\cdot^{\circ}\text{C})$ is the (ρ) $(\rho.\gamma\gamma \times 10^{\xi} \text{ ohm} \cdot \text{cm})$ and after this point is stay constant . In polymer (L1.8PDC) when the ($\log \rho$) is $(\rho.\gamma\gamma\gamma)$ in $(\gamma\cdot^{\circ}\text{C})$ is the (ρ) $(1.\rho\cdot \times 10^{\rho} \text{ ohm} \cdot \text{cm})$ and after this point is stay constant . Also we notice the conductivity of polymer (LPDC) high than conductivity of polymers (L1.4PDC, L1.8PDC) this due to quantity of carbon black adding in polymer (LPDC) is more than the rest ,also due to morphologic changes when happen on heating and molecular moving changes for polymers chain or some part it , or happen cross linking reaction between polyethylene and other compounds⁽³⁰⁾ .

Fig.(3-8) show the log permittivity ($\log \epsilon$) with the temperature ($^{\circ}\text{C}$) for to polymers prepared (LPDC ,L1.4PDC, L1.8PDC) , when we notice ($\log \epsilon$) for LPDC polymer begin increase for to temperature ($\rho\cdot^{\circ}\text{C}$) and stay constant ,when ($\log \epsilon$) for LPDC polymer in $(\rho\cdot^{\circ}\text{C})$ $(\gamma.\xi\cdot)$ is the (ϵ) $(\gamma.\gamma\gamma \times 10^{\gamma})$ while notice ($\log \epsilon$) for (L1.4PDC, L1.8PDC) polymers begin increase for to temperature

(70 °C) and stay constant ,when (log ϵ) for (L1.4PDC, L1.4PDC) polymers in (70 °C) (1.940 , 1.377) is the (ϵ) (8.81 \times 10¹ , 2.38 \times 10¹) , we notice the dielectric constant or permittivity for above polymers increase for additive increase for polyethylene .

Fig.(3-9) shows the resistivity(ρ) of prepared polymer (L1.4PDC+G1) [Table (3-9) page 68] with the time at different temperature .Its clearly noticed that the resistivity() value decreases with increasing temperature , its value were [0.06 \times 10⁶ , 3.98 \times 10⁶ , 1.04 \times 10⁶ , 1.79 \times 10⁶ , 1.90 \times 10⁶ , 1.90 \times 10⁶ and 1.98 \times 10⁶ ohm.cm] at temperature [27, 40, 50, 70, 90, 100 and 110 °C] respectively . The resistivity() value increased with the time up to (20 min.) and then level off at (27 °C) . While about same trends were noticed for others temperature i.e. no change ()of with time. This is may be due to for annealing or creastilaization on heating of polyethylene (202-204) .

The behavior polymer(L1.4PDC+G1) permittivity (ϵ) with the time in different temperature is shown in Fig.(3-10) . Where the permittivity (ϵ) remain constant with time up to (80 min.) and then remain constant except at (27 , 70 °C) a fluctuation behavior was noticed which could be due to for annealing or creastilaization on heating of polyethylene (202-204) .

Fig.(3-11) shows the resistivity(ρ) of prepared polymer (L1.4PDC) [Table (3-8) page 68] with the time at different temperature .Its clearly noticed that the resistivity() value decreases with increasing temperature , its value were

[3.74×10^7 , 3.74×10^7 , 4.1×10^7 , 4.4×10^8 , 6.78×10^8 , 6.06×10^8 and 7.00×10^8 ohm.cm] at temperature [27, 30, 37, 40, 50 and 55 °C] respectively . The resistivity(ρ) value increased with the time up to (8 min.) and then level off at (55 °C) . While about same trends were noticed for others temperature i.e. no change (ρ) of with time except at (37 °C) where a decreases up to (10 min.) then level off . This is may be due to for annealing or crystallization on heating of polyethylene in temperature less than melting point (T_m)⁽²⁰²⁻²⁰⁴⁾ .

The behavior polymer(**LPDC**) permittivity (ϵ) with the time in different temperature is shown in Fig.(3-12). Where the permittivity (ϵ) remain constant with time up to (10 min.) and then remain constant except at (27, 30 °C) a fluctuation behavior was noticed which could be due to for annealing or crystallization on heating of polyethylene in temperature less than melting point (T_m)⁽²⁰²⁻²⁰⁴⁾ .

Fig.(3-13) shows the resistivity(ρ) of prepared polymer (**LPDC-G1**) [Table (2-9) page 68] with the time at different temperature. Its clearly noticed that the resistivity(ρ) value decreases with increasing temperature , its value were [1.20×10^7 , 1.21×10^7 , 1.18×10^7 , 1.06×10^8 , 1.11×10^8 , 1.09×10^8 and 1.11×10^8 ohm.cm] at temperature [27, 30, 37, 40, 50 and 55 °C] respectively . The resistivity(ρ) value decreased with the time up to (8 min.) and then level off at (27 °C) . While about same trends were noticed for others temperature i.e.

no change () of with time except at (70 °C) where a increases up to (70 min.) then level off. This is may be due to for happens of molecular orientation type ,annealing or creastilaization of polymers⁽²⁰²⁻²⁰⁴⁾.

The behavior polymer(LPDCrG) permittivity (ε) with the time in different temperature is shown in Fig.(3-14). Where the permittivity (ε) decreased with time up to (90 min.) and then remain constant except at (70, 90 °C) a increases up to (70 min.) then level off, was noticed which could be due to for happens of molecular orientation type ,annealing or creastilaization of polymers⁽²⁰²⁻²⁰⁴⁾.

Fig. (3-15) show the log resistivity (log ρ) with the temperature (°C) for to polymers prepared (L1.8PDCrG, L1.4PDCrG, LPDCrG) we notice the temperature increase the (log ρ) is decrease this meāning the conductivity is increase for three polymers. In polymer (L1.8PDCrG) when the (log ρ) is (0.296) in (70 °C) is the () ρ (1.98 × 10⁹ ohm . cm) and after this point is stay constant. In polymer (L1.4PDCrG) when the (log ρ) is (4.602) in (70 °C) is the () ρ (4.49 × 10⁴ ohm^ρ . cm) and after this point is stay constant. In polymer (LPDCrG) when the (log ρ) is (0.040) in (70 °C) is the () ρ (1.11 × 10⁹ ohm . cm) and after this point is stay constant. Also we notice the conductivity of polymer (L1.4PDCrG) high than conductivity of polymer (LPDCrG) and this high than conductivity (L1.8PDCrG) this due to quantity of carbon black and graphite adding to polymer, also due to morphologic changes when happen on heating treatment and molecular moving changes for polymers chain or some part it, or happen cross linking reaction between

polyethylene and other compounds⁽²⁶⁾. This can be related to the fact that at this region the composites conductivity depends strongly on the filler conductivity. The graphite has a conductivity in the order of (10^4 S/cm) while the carbon black has a conductivity in the order of (10^2 S/cm)⁽²⁰⁾.

Fig. (3-16) shows the log permittivity ($\log \epsilon$) with the temperature ($^{\circ}\text{C}$) for the polymers prepared (L1.8PDCrG1 , L1.4PDCrG1 , LPDCrG1), when we notice ($\log \epsilon$) for (L1.8PDCrG1) polymer begins to increase for the temperature (50°C) and stays constant, the ($\log \epsilon$) in (70°C) (1.428) is the (ϵ) (2.68×10) while we notice ($\log \epsilon$) for (L1.4PDCrG1) polymer begins to increase for the temperature (50°C) and stays constant, the ($\log \epsilon$) in (70°C) (1.691) is the (ϵ) (4.92×10^2) while we notice ($\log \epsilon$) for (LPDCrG1) polymer begins to increase for the temperature (50°C) and stays constant, the ($\log \epsilon$) in (70°C) (1.026) is the (ϵ) (3.36×10), the dielectric constant or permittivity for the above polymers depends on the quantity percentage of carbon black and graphite with other compounds.

Fig. (3-17) shows the resistivity (ρ) of prepared polymer (L1.8PDCrG) [Table (2-10) page 19] with the time at different temperatures. It is clearly noticed that the resistivity (ρ) value decreases with increasing temperature, its values were [1.18×10^7 , 1.18×10^7 , 1.18×10^7 , 1.29×10^6 , 1.21×10^6 , 1.20×10^6 and 1.29×10^6 ohm.cm] at temperatures [$27, 40, 50, 70, 90, 100$ and 110°C]

ρ

respectively. The resistivity (ρ) value increased with the time up to (60 min.) and then level off at (90 °C). While about same trends were noticed for others temperature i.e. no change (ρ) of with time except at (110 °C) where a decreases up to (60 min.) then level off. This is may be due to for annealing or creastilaization on heating of polyethylene⁽²⁰²⁻²⁰⁴⁾.

The behavior polymer (L1-PDCG) permittivity (ϵ) with the time in different temperature is shown in Fig.(3-18). Where the permittivity (ϵ) remain constant with time up to (60 min.) and then remain constant except at (90, 100, 110 °C) a fluctuation behavior was noticed which could be due to for annealing or creastilaization on heating of polyethylene⁽²⁰²⁻²⁰⁴⁾.

Fig.(3-19) shows the resistivity (ρ) of prepared polymer (L1-PDCG) [Table (2-10) page 69] with the time at different temperature. Its clearly noticed that the resistivity (ρ) value increases with increasing temperature, its value were [1.29×10^7 , 1.28×10^7 , 1.29×10^7 , 1.33×10^8 , 1.20×10^8 , 1.29×10^8 and 1.33×10^8 ohm.cm] at temperature [29, 40, 50, 70, 90, 100 and 110 °C] respectively. The resistivity (ρ) value increased with the time up to (40 min.) and then level off at (29 °C). While about same trends were noticed for others temperature i.e. no change (ρ) of with time except at (110 °C) where a decreases up to (60 min.) then level off. This is may be due to for annealing or creastilaization on heating of polyethylene in temperature less than melting point (Tm)⁽²⁰²⁻²⁰⁴⁾.

The behavior polymer(**LPDCG**) permittivity (ϵ) with the time in different temperature is shown in Fig.(3-20). Where the permittivity (ϵ) decreases with time up to (10 min.) and then remain constant except at (29, 40, 50 °C) a fluctuation behavior was noticed which could be due to for annealing or creastilaization on heating of polyethylene in temperature less than melting point (T_m)⁽²⁰²⁻²⁰⁴⁾ .

Fig.(3-21) shows the resistivity(ρ) of prepared polymer (**LPDCG**) [Table (2-10) page 69] with the time at different temperature .Its clearly noticed that the resistivity(ρ) value increases with increasing temperature , its value were [1.31×10^7 , 1.29×10^7 , 1.38×10^7 , 1.29×10^7 , 1.20×10^7 , 1.33×10^7 and 1.29×10^7 ohm.cm] at temperature [28, 40, 50, 70, 90, 100 and 110 °C] respectively . The resistivity(ρ) value increased with the time up to (10 min.) and then level off at (28 °C) . While about same trends were noticed for others temperature i.e. no change (ρ)of with time except at (50 °C) where a decreases up to (10 min.) then level off . This is may be due to for annealing or creastilaization on heating of polyethylene⁽²⁰²⁻²⁰⁴⁾ .

The behavior polymer(**LPDCG**) permittivity (ϵ) with the time in different temperature is shown in Fig.(3-22). Where the permittivity (ϵ) increases with time up to (10 min.) and then remain constant except at (70, 90, 100, 110 °C) a fluctuation behavior was noticed which could be due to for annealing or creastilaization on heating of polyethylene⁽²⁴³⁻²⁴⁵⁾ .

Fig. (3-23) show the log resistivity ($\log \rho$) with the temperature ($^{\circ}\text{C}$) for to polymers prepared (**L_{1.1}PDCG**, **L_{1.4}PDCG**, **LPDCG**) we notice the temperature increase the ($\log \rho$) is decrease this meaning the conductivity is increase for three polymers. In polymer (**L_{1.1}PDCG**) when the ($\log \rho$) is (0.136) in ($^{\circ}\text{C}$) is the (ρ) ($1.37 \times 10^{\circ}$ ohm . cm) and after this point is stay constant. In polymer (**L_{1.4}PDCG**) when the ($\log \rho$) is (0.110) in ($^{\circ}\text{C}$) is the (ρ) ($1.29 \times 10^{\circ}$ ohm . cm) and after this point is stay constant. In polymer (**LPDCG**) when the ($\log \rho$) is (0.142) in ($^{\circ}\text{C}$) is the (ρ) ($1.39 \times 10^{\circ}$ ohm . cm) and after this point is stay constant. We notice the conductivity of polymers (**L_{1.1}PDCG**, **L_{1.4}PDCG**, **LPDCG**) is approximation equals, this due to quantity of carbon black and graphite is equal at in three polymers when the conductivity of polymers due to morphologic changes when happen on heating treatment and molecular moving changes for polymers chain or some part it (201).

Fig. (3-24) show the log permittivity ($\log \epsilon$) with the temperature ($^{\circ}\text{C}$) for to polymers prepared (**L_{1.1}PDCG**, **L_{1.4}PDCG**, **LPDCG**), when we notice ($\log \epsilon$) for (**L_{1.1}PDCG**) polymer begin increase for to temperature ($^{\circ}\text{C}$) and stay constant, the ($\log \epsilon$) in ($^{\circ}\text{C}$) (2.026) is the (ϵ) (3.36×10^2) also notice ($\log \epsilon$) for (**L_{1.4}PDCG**) polymer begin increase for to temperature ($^{\circ}\text{C}$) and stay constant, the ($\log \epsilon$) in ($^{\circ}\text{C}$) (2.004) is the (ϵ) (3.19×10^2) while notice ($\log \epsilon$) for (**LPDCG**) polymer begin increase for to temperature ($^{\circ}\text{C}$) and stay constant, the ($\log \epsilon$) in ($^{\circ}\text{C}$) (2.011) is the (ϵ) (3.20×10^2), the dielectric constant or permittivity for above polymers is approximation equals

, this due to quantity of carbon black and graphite is equals on three polymers .

Fig.(3-25) shows the resistivity(ρ) of prepared polymer (**L_{1.1}PDC₁G_r**) [Table (2-11) page 69] with the time at different temperature .Its clearly noticed that the resistivity(ρ) value increases with increasing temperature , its value were [1.16×10^7 , 1.14×10^7 , 1.2×10^7 , 1.37×10^8 , 1.43×10^8 , 1.38×10^8 and 1.38×10^8 ohm.cm] at temperature [$30, 40, 50, 70, 90, 100$ and 110 °C] respectively . The resistivity(ρ) value increased with the time up to (8 min.) and then level off at (30 °C) . While about same trends were noticed for others temperature i.e. no change (ρ) of with time except at (90 °C) a fluctuation behavior then level off . This is may be due to for annealing or creastilaization on heating of polyethylene⁽²⁰²⁻²⁰⁴⁾ .

The behavior polymer(**L_{1.1}PDC₁G_r**) permittivity (ϵ) with the time in different temperature is shown in Fig.(3-26). Where the permittivity (ϵ) increases with time up to (8 min.) and then remain constant except at (90 °C) a fluctuation behavior was noticed which could be due to for annealing or creastilaization on heating of polyethylene⁽²⁰²⁻²⁰⁴⁾ .

Fig.(3-27) shows the resistivity(ρ) of prepared polymer (**LPDC₁G_r**) [Table (2-11) page 69] with the time at different temperature .Its clearly noticed that the resistivity(ρ) value increases with increasing temperature , its value were [1.31×10^7 , 1.29×10^7 , 1.29×10^7 , 1.37×10^8 , 1.39×10^8 , 1.43×10^8 and 1.40×10^8 ohm.cm] at temperature [$29, 40, 50, 70, 90, 100$ and 110 °C] respectively . The resistivity(ρ) value increased with the time up to (4 min.)

and then level off at (29 °C) . While about same trends were noticed for others temperature i.e. no change ()of with time. This is may be due to for annealing or creastilaization on heating of polyethylene (202-204) .

The behavior polymer(LPDC,Gr) permittivity (ε) with the time in different temperature is shown in Fig.(3-28). Where the permittivity (ε) increases with time up to (9 min.) and then remain constant was noticed which could be due to for annealing or creastilaization on heating of polyethylene (202-204) .

Fig.(3-29) shows the resistivity(ρ) of prepared polymer (LPDG) [Table (2-12) page 70] with the time at different temperature .Its clearly noticed that the resistivity() value increases with increasing temperature , its value were [1.33x10⁷ , 1.4x10⁷ , 1.29x10⁷ , 6.49x10⁸ , 6.43x10⁸ , 6.06x10⁸ and 6.67x10⁸ ohm.cm] at temperature [27, 40, 50, 70, 90, 100 and 110 °C] respectively . The resistivity(ρ) value increased with the time up to (8 min.) and then level off at (27 °C) . While about same trends were noticed for others temperature i.e. no change ()of with time except at (0 °C) where a decreases up to (8 min.) then level off . This is may be due to for annealing or creastilaization on heating of polyethylene (202-204)

The behavior polymer(LPDC,Gr) permittivity (ε) with the time in different temperature is shown in Fig.(3-30). Where the permittivity (ε) increases with time up to (8 min.) and then remain constant was noticed

which could be due to for annealing or creastilaization on heating of polyethylene^(٢٥٢-٢٥٤).

Fig. (٣-٣١) show the log resistivity ($\log \rho$) with the temperature ($^{\circ}\text{C}$) for to polymers prepared (**L_{1.5}PDC₁G_r**, **LPDC₁G_r**, **LPDG**) we notice the temperature increase the ($\log \rho$) is decrease this meaning the conductivity is increase for three polymers .In polymer (**L_{1.5}PDC₁G_r**) when the ($\log \rho$) is (٥.١٥٤) in (٧٠°C) is the (ρ) ($١.٤٣ \times ١٠^{\circ}$ ohm . cm) and after this point is stay constant . In polymer (**LPDC₁G_r**) when the ($\log \rho$) is (٥.١٧٠) in (٧٠°C) is the (ρ) ($١.٤٨ \times ١٠^{\circ}$ ohm . cm) and after this point is stay constant . In polymer (**LPDG**) when the ($\log \rho$) is (٤.٨٢٢) in (٧٠°C) is the (ρ) ($٦.٦٤ \times ١٠^{\circ}$ ohm . cm) and after this point is stay constant . We notice the conductivity of polymer (**LPDG**) is high than the conductivity of polymers (**L_{1.5}PDC₁G_r**, **LPDC₁G_r**) , when this due to the conductivity of graphite in polymer (**LPDG**) without carbon black , while in polymers (**L_{1.5}PDC₁G_r**, **LPDC₁G_r**) the graphite less than quantity from (**LPDG**) polymer also due to morphologic changes when happen on heating treatment and molecular moving changes for polymers chain or some part it or happen cross linking reaction between polyethylene and other compounds^(٢٥١) .

Fig. (٣-٣٢) show the log permittivity ($\log \epsilon$) with the temperature ($^{\circ}\text{C}$) for to polymers prepared (**L_{1.5}PDC₁G_r**, **LPDC₁G_r**, **LPDG**) , when we notice ($\log \epsilon$)

for (L₁,^ΛPDC\G_r) polymer begin increase for to temperature (70 °C) and stay constant ,the (log ε) in (70 °C) (2.033) is the (ε) (3.42 × 10⁷) also notice (log ε) for (LPDC\G_r) polymer begin increase for to temperature (70 °C) and stay constant ,the (log ε) in (70 °C) (2.031) is the (ε) (3.40 × 10⁷) while notice (log ε) for (LPDG) polymer begin increase for to temperature (70 °C) and stay constant ,the (log ε) in (70 °C) (2.404) is the (ε) (2.04 × 10⁷) , the dielectric constant or permittivity for (LPDG) polymer is differ from other polymers (L₁,^ΛPDC\G_r ,LPDC\G_r) , this due to quantity additive addition from carbon black and graphite to polymers

Fig.(3-33) shows the resistivity(ρ) of prepared polymer (H₁,^ΛPDCG) [Table (2-13) page 70] with the time at different temperature .Its clearly noticed that the resistivity(ρ) value increases with increasing temperature , its value were [3.01 × 10⁷ , 3.00 × 10⁷ , 3.02 × 10⁷ , 3.74 × 10⁸ , 3.77 × 10⁸ , 3.80 × 10⁸ and 3.81 × 10⁸ ohm.cm] at temperature [30, 40, 50, 70, 90, 100 and 110 °C] respectively . The resistivity(ρ) value increased with the time up to (60 min.) and then level off at (70 °C) . While about same trends were noticed for others temperature i.e. no change (ρ) of with time except at (40 °C) a fluctuation behavior then level off. This is may be due to for annealing or creastilaization on heating of polyethylene⁽²⁰²⁻²⁰⁴⁾ .

The behavior polymer(H₁,^ΛPDCG) permittivity (ε) with the time in different temperature is shown in Fig.(3-34). Where the permittivity (ε)

increases with time up to (10 min.) and then remain constant except at (100°C) a fluctuation behavior was noticed which could be due to for annealing or creastilaization on heating of polyethylene⁽²⁰²⁻²⁰⁴⁾.

Fig.(3-30) shows the resistivity(ρ) of prepared polymer (**H₁PCDG**) [Table (2-13) page 10] with the time at different temperature .Its clearly noticed that the resistivity(ρ) value increases with increasing temperature , its value were [3.10×10^6 , 3.17×10^6 , 3.20×10^6 , 7.22×10^8 , 7.00×10^8 , 7.69×10^8 and 7.78×10^8 ohm.cm] at temperature [27, 40, 50, 70 , 90, 100 and 110 °C] respectively . The resistivity(ρ) value increased with the time up to (10 min.) and then level off at (27 °C) . While about same trends were noticed for others temperature i.e. no change (ρ) of with time . This is may be due to for annealing or creastilaization on heating of polyethylene⁽²⁰²⁻²⁰⁴⁾ .

The behavior polymer(**H₁PCDG**) permittivity (ϵ) with the time in different temperature is shown in Fig.(3-31). Where the permittivity (ϵ) increases with time up to (10 min.) and then remain constant was noticed which could be due to for annealing or creastilaization on heating of polyethylene⁽²⁰²⁻²⁰⁴⁾ .

Fig.(3-32) shows the resistivity(ρ) of prepared polymer (**HPDCG**) [Table (2-13) page 10] with the time at different temperature .Its clearly noticed that the resistivity(ρ) value increases with increasing temperature , its value were [3.00×10^6 , 3.08×10^6 , 3.10×10^6 , 0.21×10^8 , 0.28×10^8 , 0.41×10^8

and 0.43×10^4 ohm.cm] at temperature [29, 40, 50, 70, 90, 100 and 110 °C] respectively. The resistivity () value increased with the time up to (60 min.) and then level off at (29 °C). While about same trends were noticed for others temperature i.e. no change () of with time. This is may be due to for annealing or creastilaization on heating of polyethylene⁽²⁰²⁻²⁰⁴⁾.

The behavior polymer(**HPDCG**) permittivity (**ε**) with the time in different temperature is shown in Fig.(3-38). Where the permittivity (**ε**) increases with time up to (60 min.) and then remain constant except at (29 °C) a fluctuation behavior was noticed which could be due to for annealing or creastilaization on heating of polyethylene⁽²⁰²⁻²⁰⁴⁾.

Fig. (3-39) show the log resistivity (log) with the temperature (°C) for to polymers prepared (**H_{1.8}PDCG**, **H_{1.4}PDCG**, **HPDCG**) we notice the temperature increase the (log) is decrease this meaning the conductivity is increase for three polymers. In polymer (**H_{1.8}PDCG**) when the (log) is (4.079) in (70 °C) is the () (1.8×10^4 ohm . cm) and after this point is stay constant. In polymer (**H_{1.4}PDCG**) when the (log) is (4.869) in (70 °C) is the () (7.4×10^4 ohm . cm)^ρ and after this point is stay constant. In polymer (**HPDCG**) when the (log) is (4.726) in (70 °C) is the () (0.33×10^4 ohm . cm)^ρ and after this point is stay constant. We notice the conductivity of polymer (**H_{1.8}PDCG**) is high than the conductivity of polymers (**H_{1.4}PDCG**, **HPDCG**), when this due to quantity of additives (PVC + DOP +C +G) to **HDPE** in polymer (**H_{1.8}PDCG**) more than the quantity in polymers (**H_{1.4}PDCG**, **HPDCG**), also due to morphologic changes when happen on heating treatment and molecular moving changes for polymers chain or some part it or happen cross linking reaction between polyethylene and other compounds⁽²⁰¹⁾.

Fig. (3-40) show the log permittivity ($\log \epsilon$) with the temperature ($^{\circ}\text{C}$) for to polymers prepared (**H_{1.8}PDCG, H_{1.4}PDCG, HPDCG**), when we notice ($\log \epsilon$) for three polymer above begin increase for to temperature ($^{\circ}\text{C}$) and stay constant, In polymer (**H_{1.8}PDCG**) the ($\log \epsilon$) in ($^{\circ}\text{C}$) (2.602) is the (ϵ) (1.0×10^4) also notice in polymer (**H_{1.4}PDCG**) the ($\log \epsilon$) in ($^{\circ}\text{C}$) (2.478) is the (ϵ) (3.0×10^4) while notice in polymer (**HPDCG**) the ($\log \epsilon$) in ($^{\circ}\text{C}$) (2.004) is the (ϵ) (3.09×10^4).

Figs. (3-41 – 3-50) show the log specific Conductive ($\log K$) with the temperature ($^{\circ}\text{K}$) for to polymers prepared (**LPDC, L_{1.4}PDC, L_{1.8}PDC, L_{1.8}PDCrG₁, L_{1.4}PDCrG₁, LPDCrG₁, L_{1.8}PDCG, L_{1.4}PDCG, LPDCG, L_{1.8}PDC₁G_r, LPDC₁G_r, LPDG, H_{1.8}PDCG, H_{1.4}PDCG, HPDCG**) respectively, when to find the slope =

$(- \Delta U / 2.303 \times R)$, According to equation

$$\log K = \log K_0 - \frac{U}{2.303 \times R \times T}$$

When to find the combination activation energy for to prepared polymers show in Table(3-1).

3-1-4- Electroplating

The prepared polymer [LPDC] which shows a conductance of (4.70×10^{-3} ohm.cm) conductance at (100°C), therefore an attempt to cover the polymer with certain element such copper . This was done by making the sheet of the polymer as cathode and a platinum (Pt) wire as anode , using an electrolysis apparatus [(BTL) Electrolytic Analysis , Japan] . It was noticed that the current flow is very low modification of the apparatus has been made changing the current meter from (mA) to one of (μA) in addition placing magnetic – heater apparatus in order of rise the temperature . Under these condition plating of (Cu) was observed on the sheets the polymer , but still very slow . We suggest for farther work to used different electrolytes beside of found a way of increase the conductivity of the polymer .

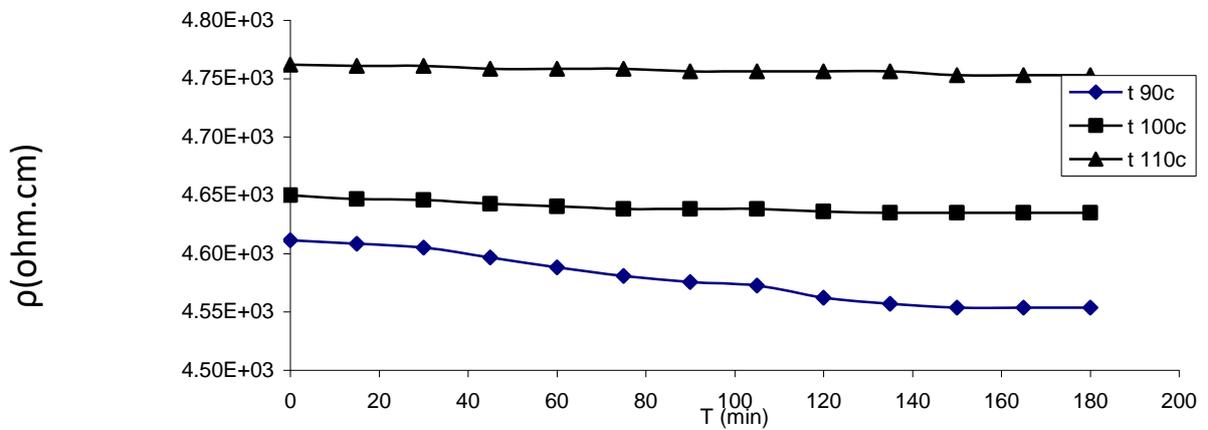
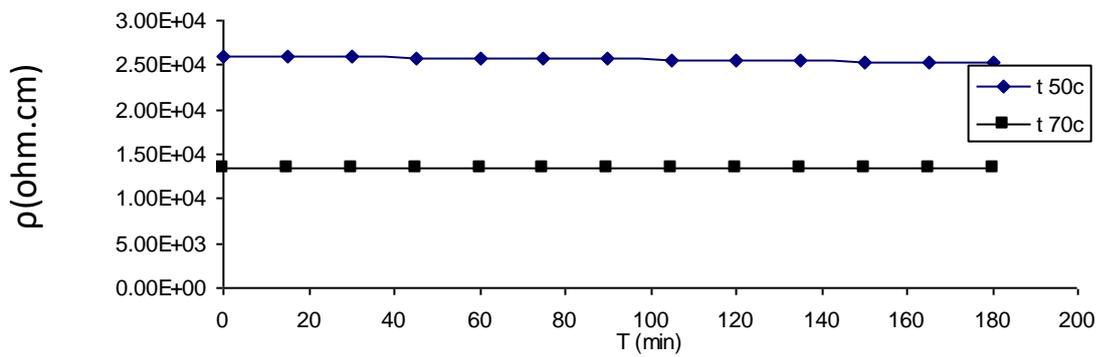
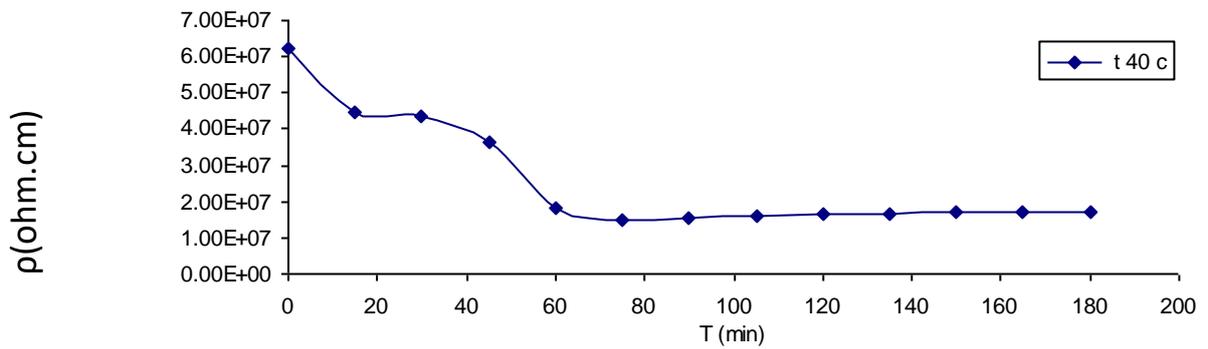
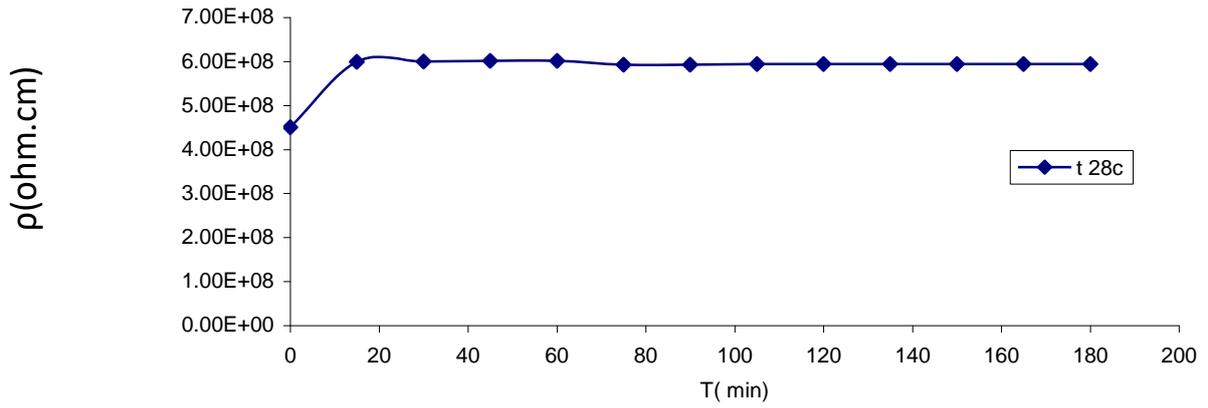
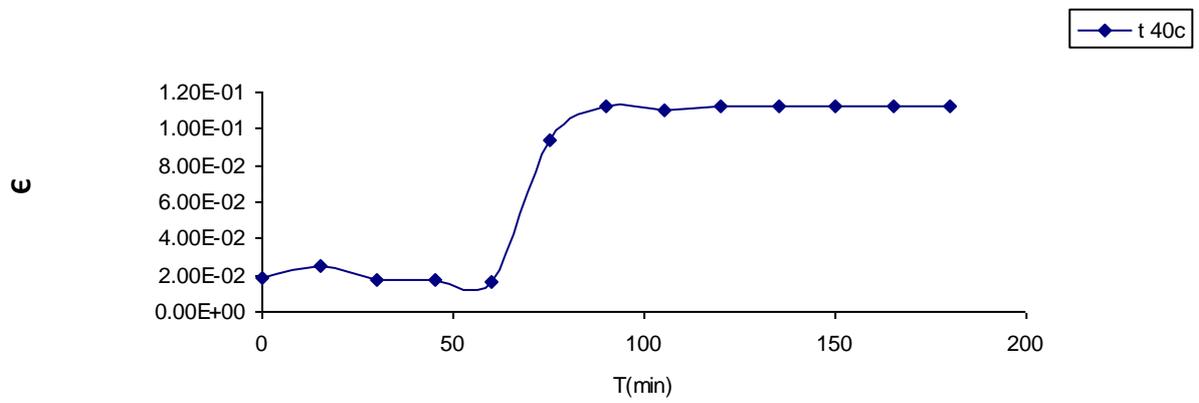
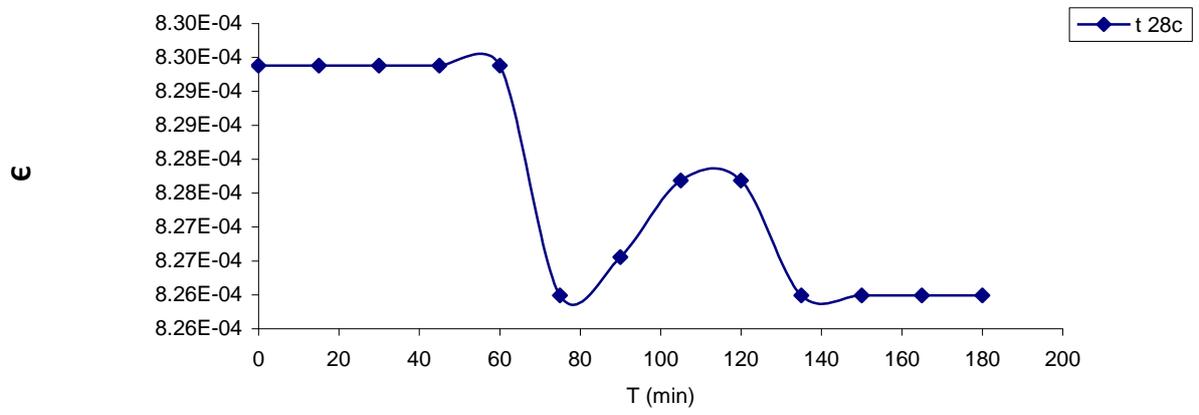


Fig.(۳-۱): Relation ship between the resistivity with the time in different temperature of (LPDC)polymer



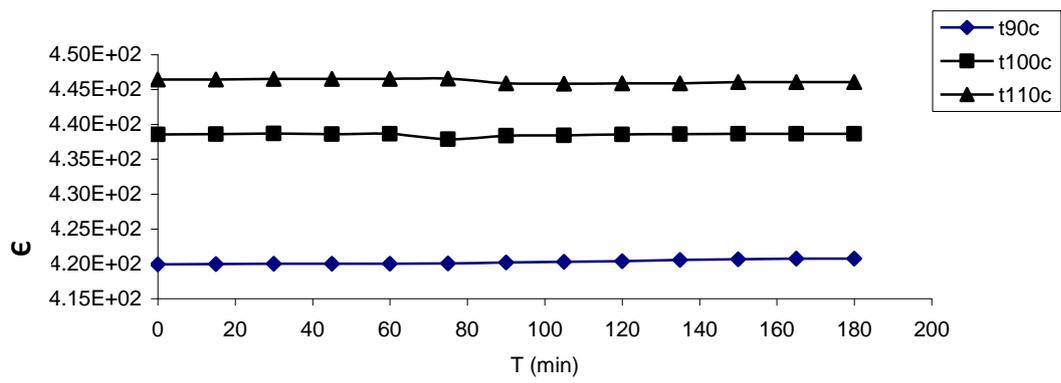
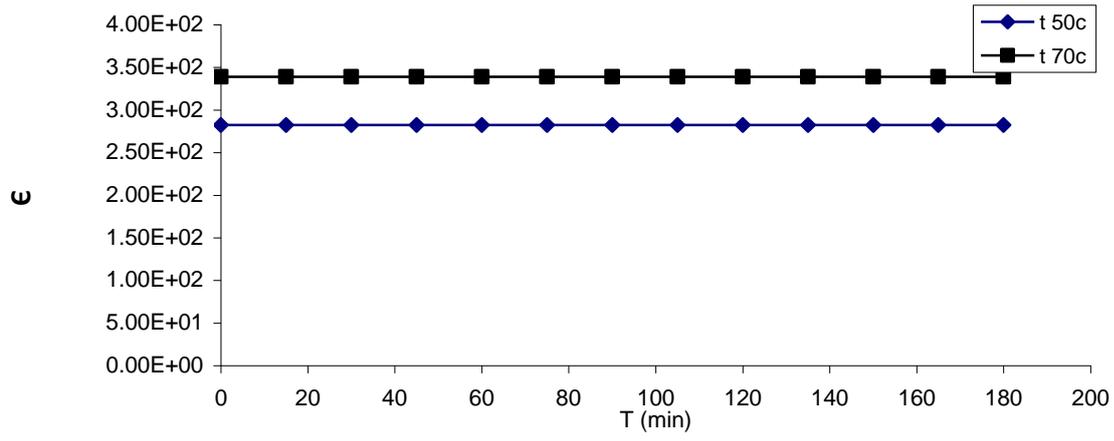


Fig.(۳-۲):

Relation ship between the permittivity with the time in different temperature of (LPDC)polymer

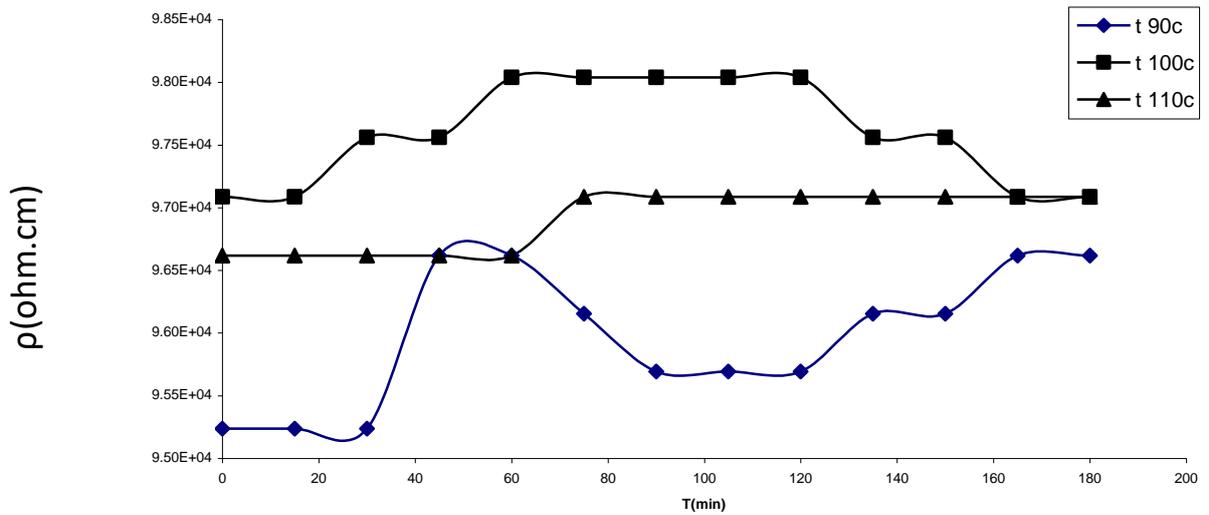
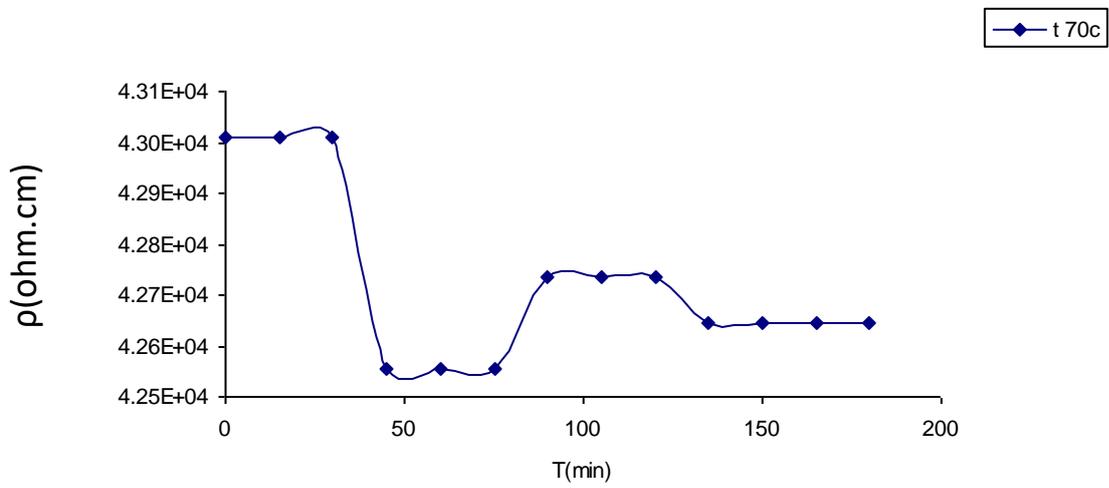
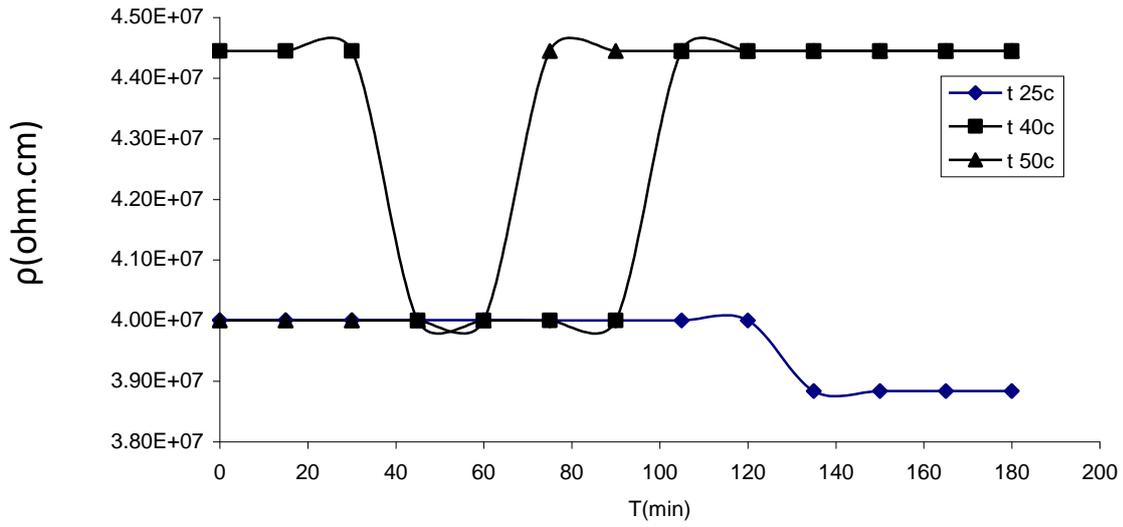
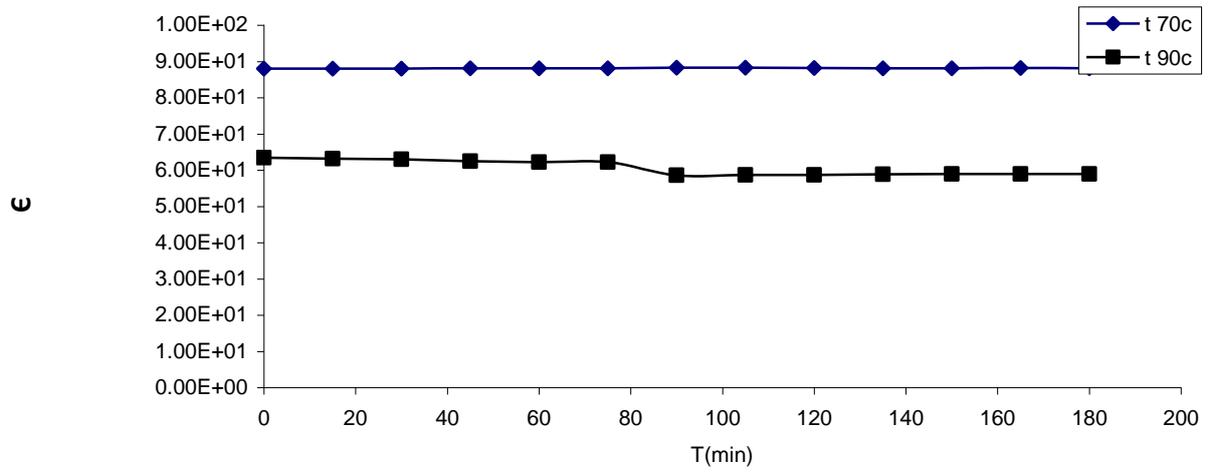
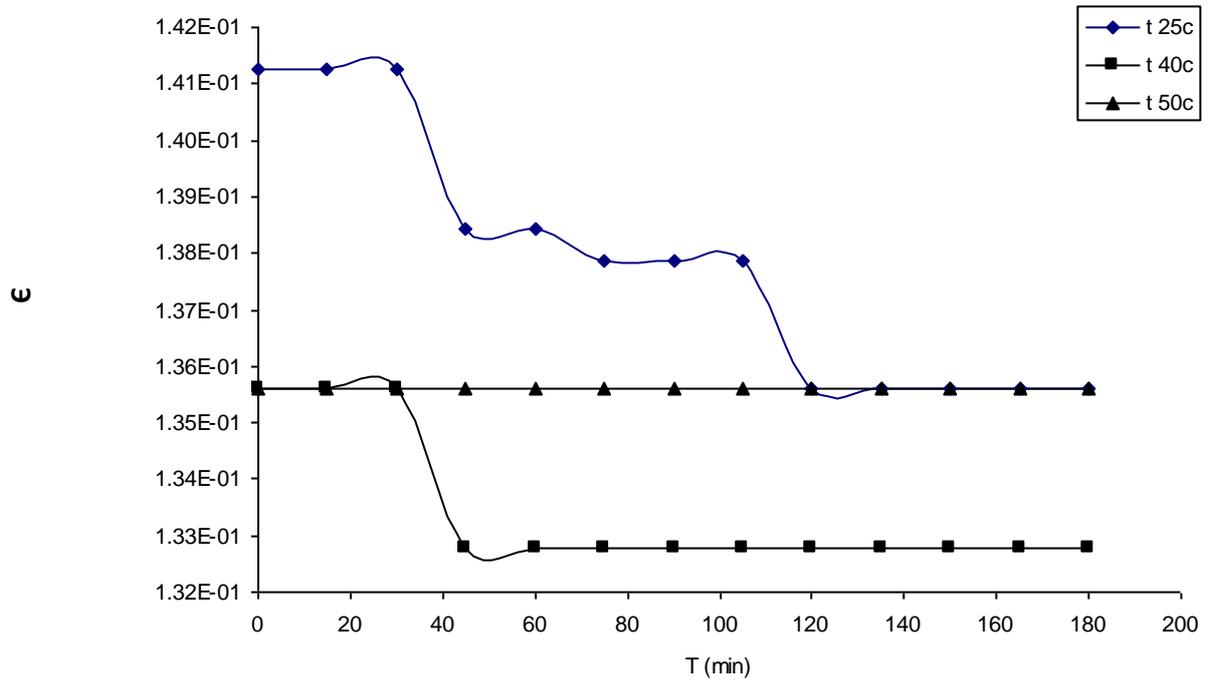


Fig.(۳-۳): Relation ship between the resistivity with the time in different temperature of (L_۱:PDC)polymer



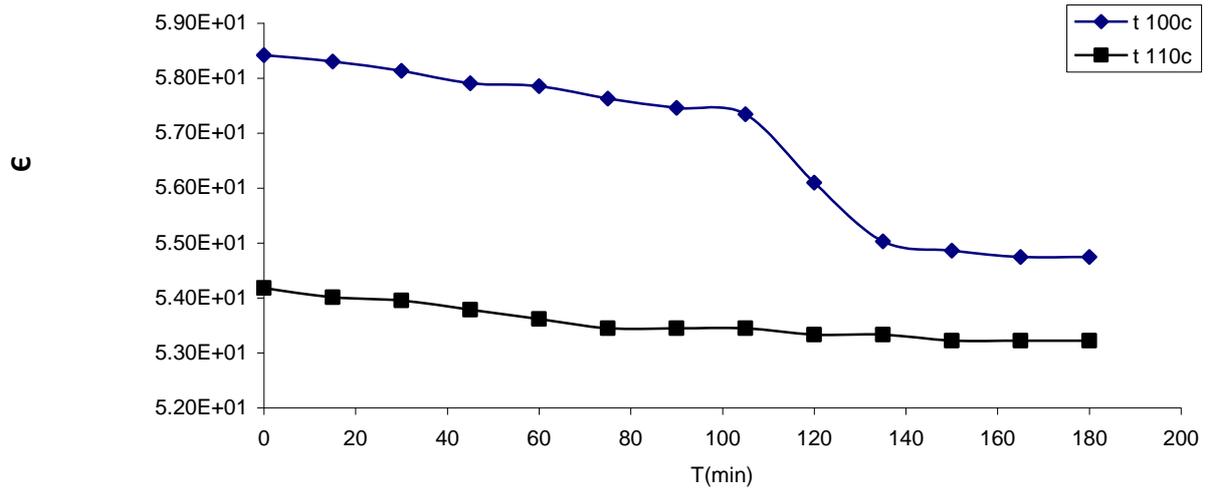
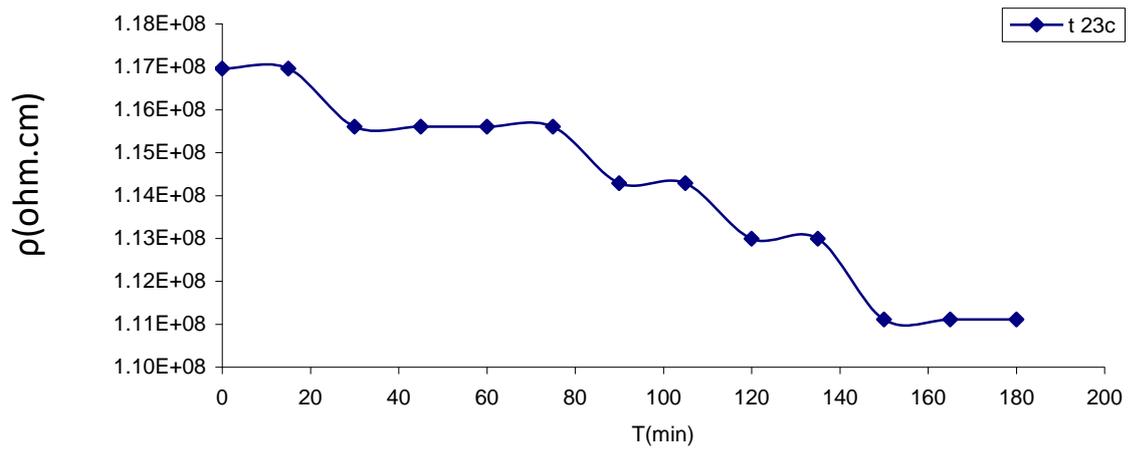


Fig.(ϵ - ϵ): Relationship between the permittivity with the time in different temperature of (L, ϵ PDC)polymer.



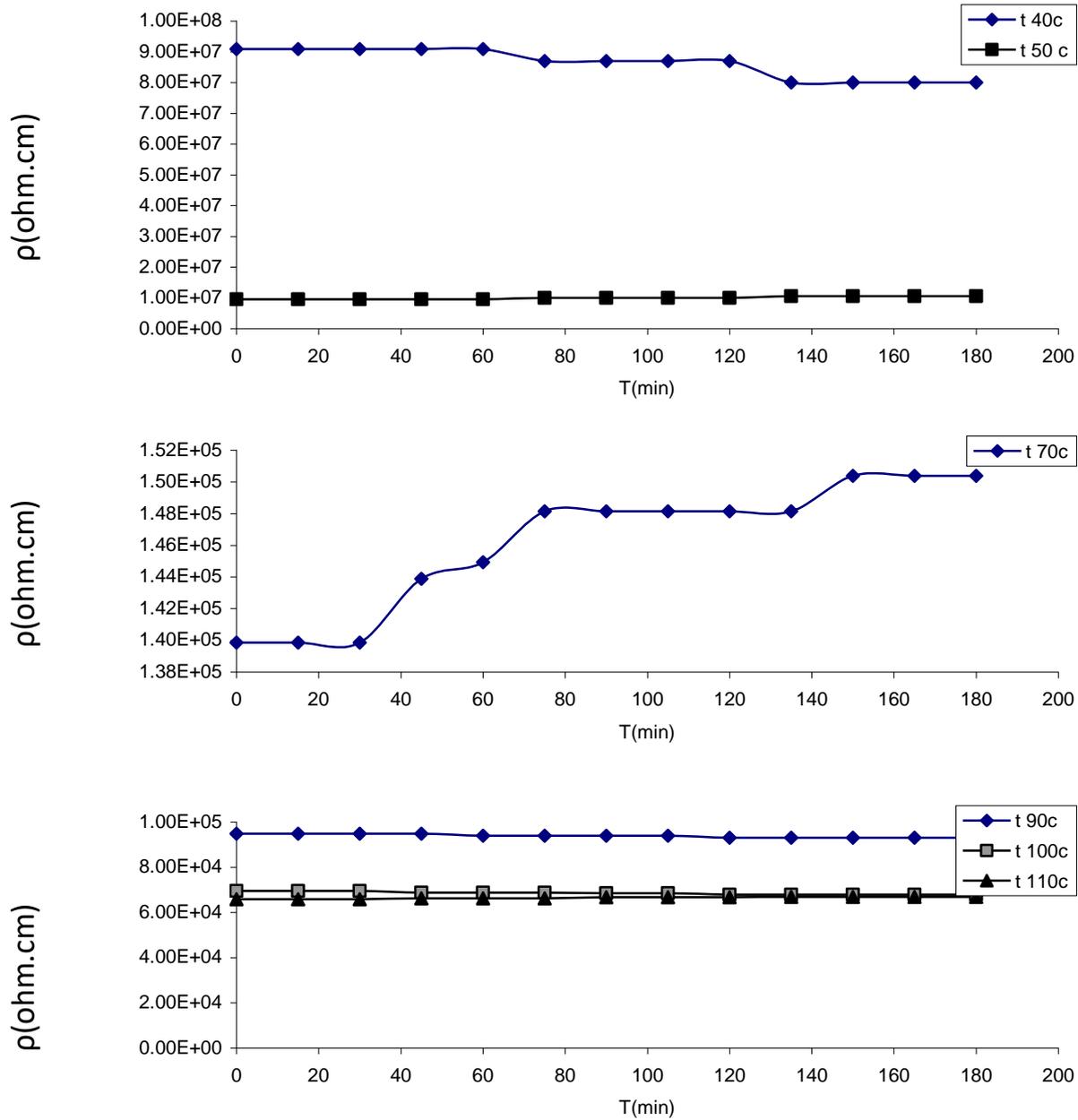


Fig.(3-9): Relation ship between the resistivity with the time in different temperature of (L_{1,4})PDC polymer

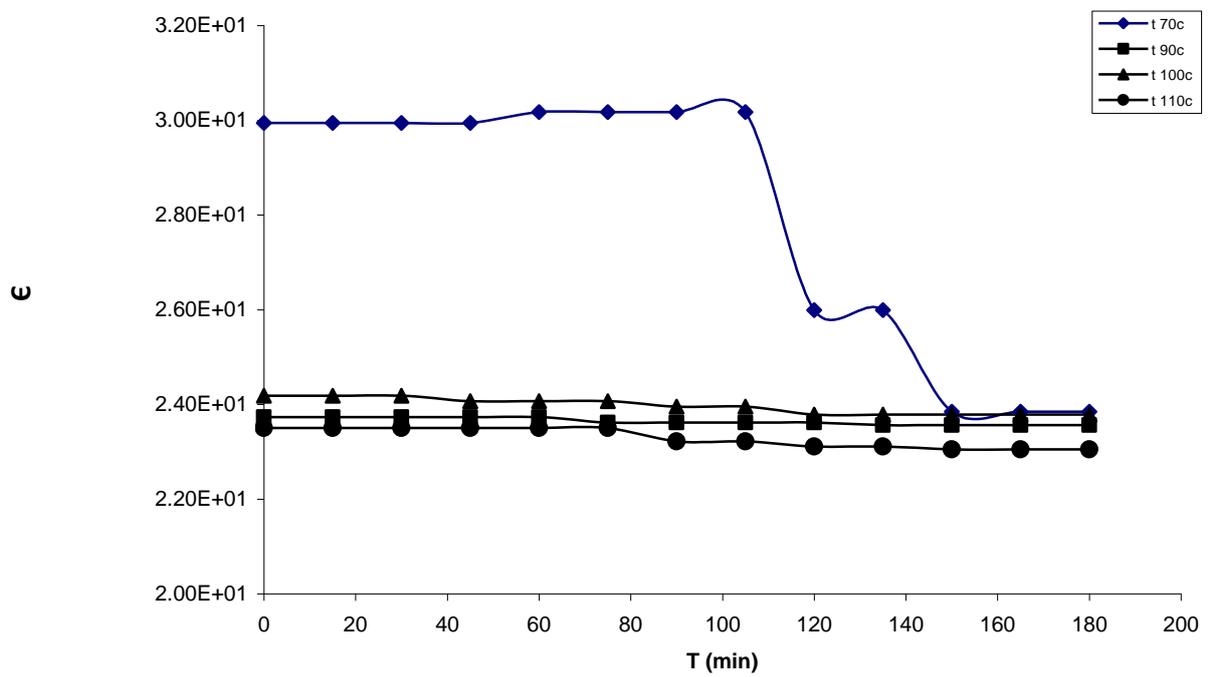
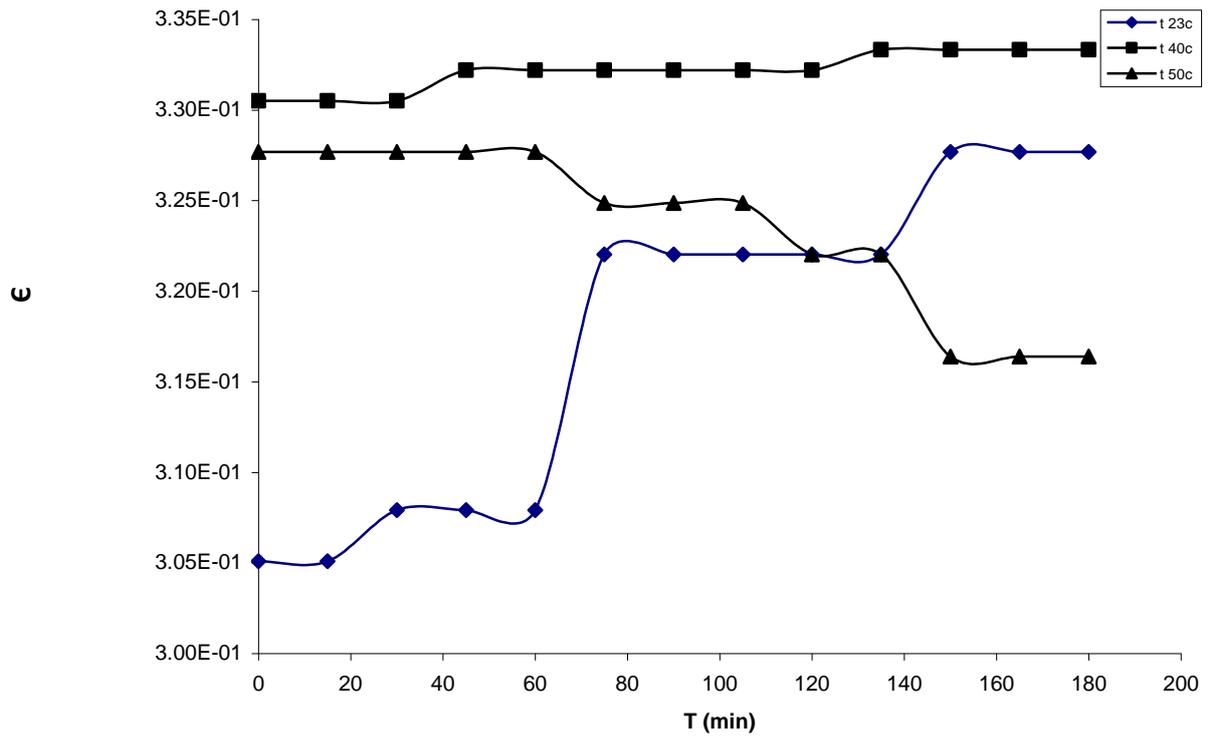
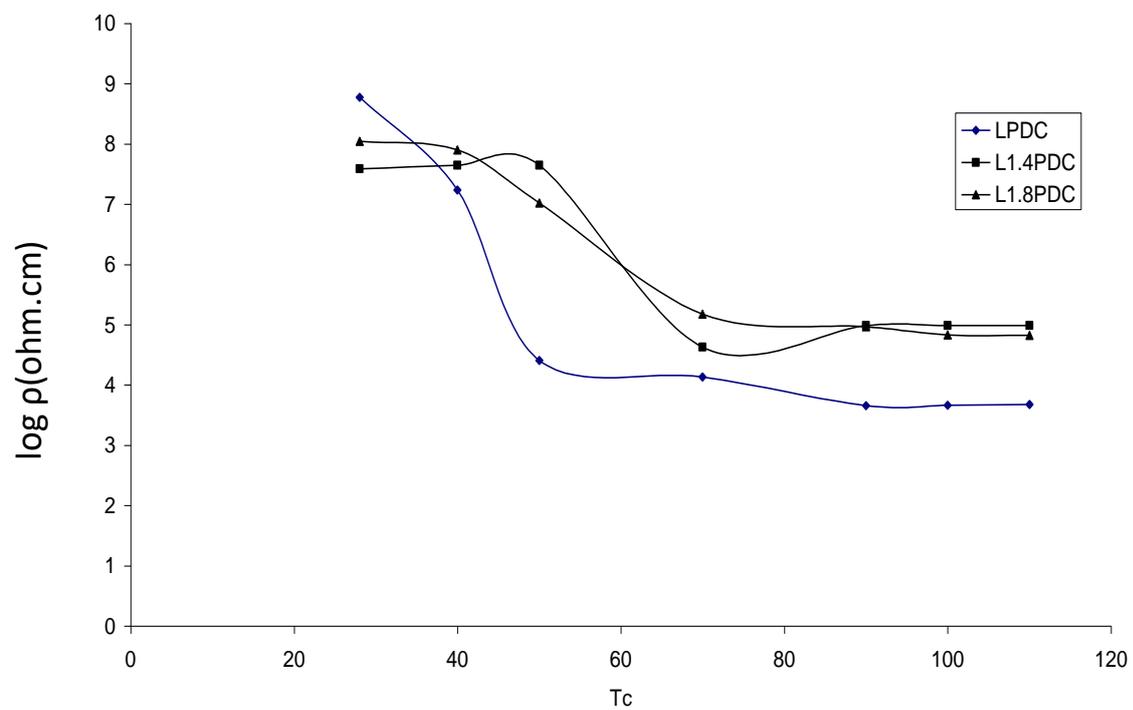
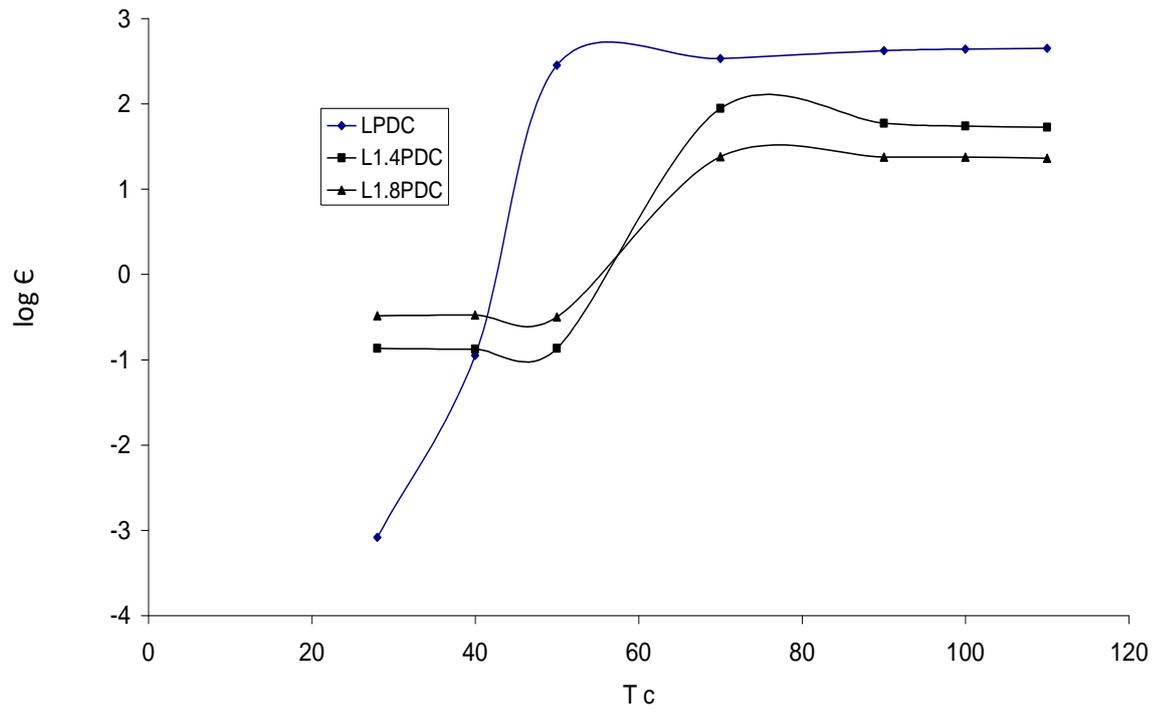


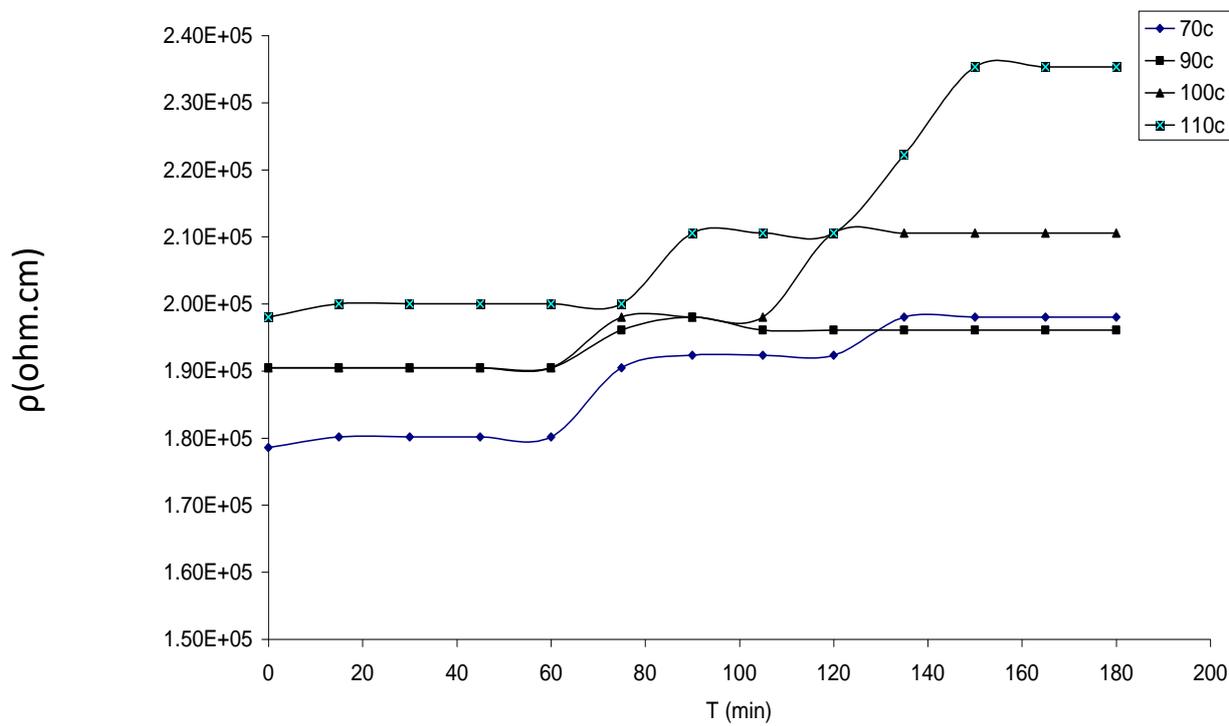
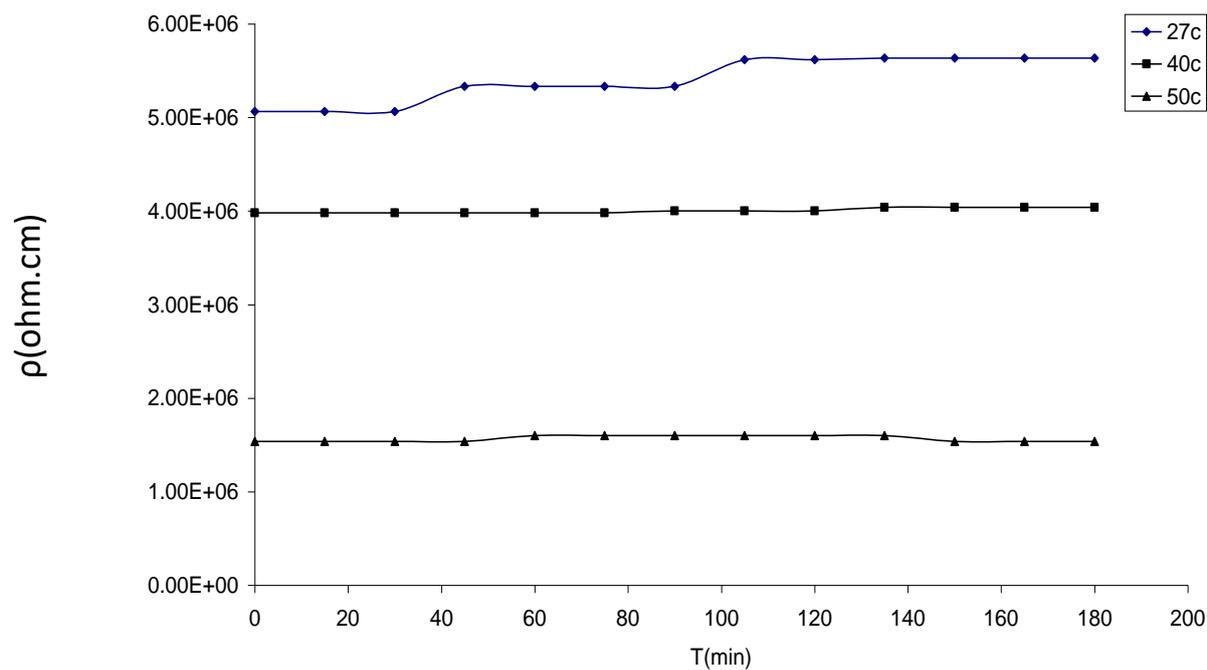
Fig.(3-1): Relationship between the permittivity with the time in different temperature of (L,γ-PDC)polymer



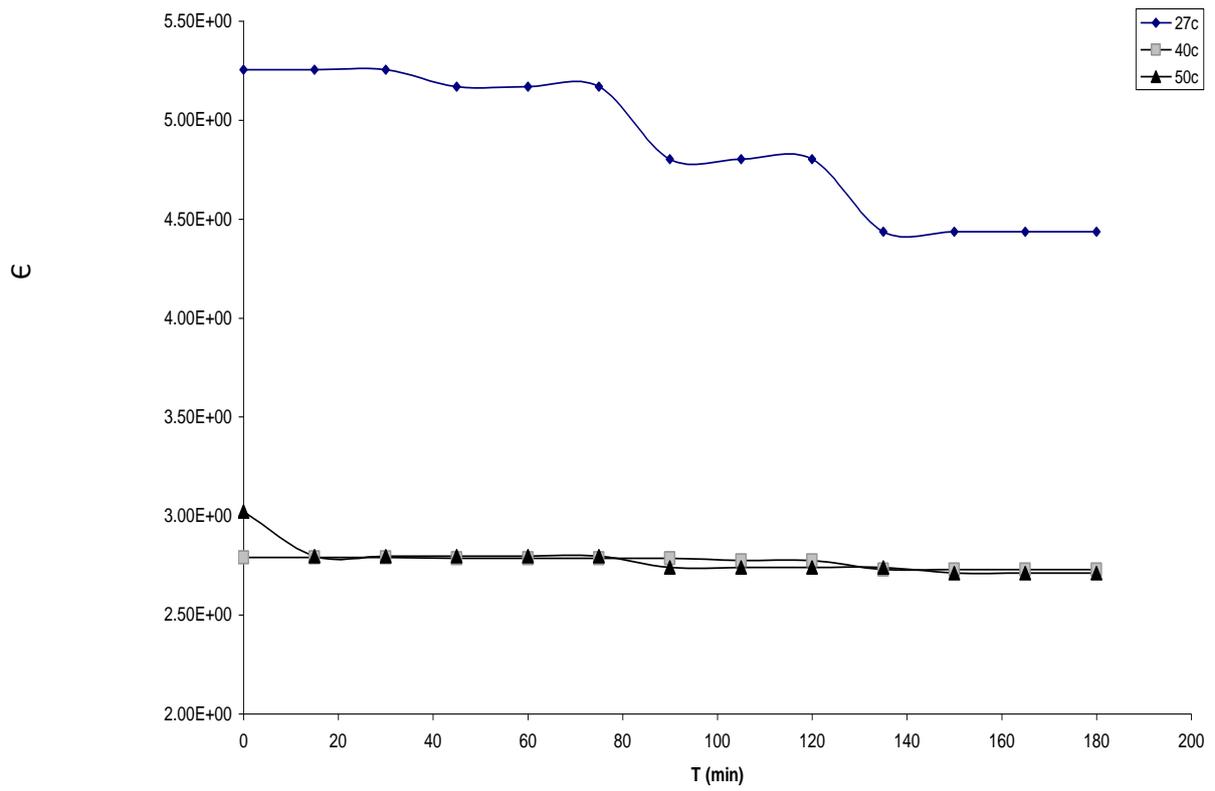
Fig(3-7): Relation ship between the resistivity with the temperature for (LPDC ,L_{1.4} PDC ,L_{1.8}PDC)polymers

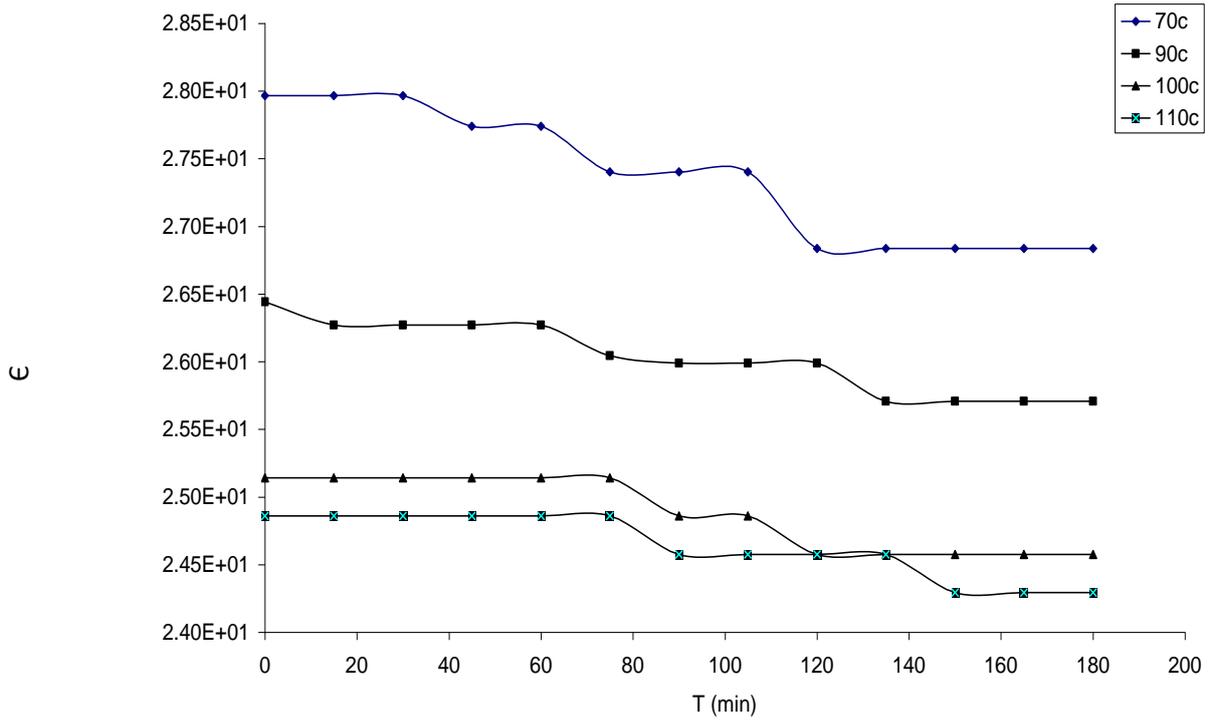


Fig(3-8): Relationship between the permittivity with the temperature for (LPDC, L1.4PDC, L1.8PDC) polymers

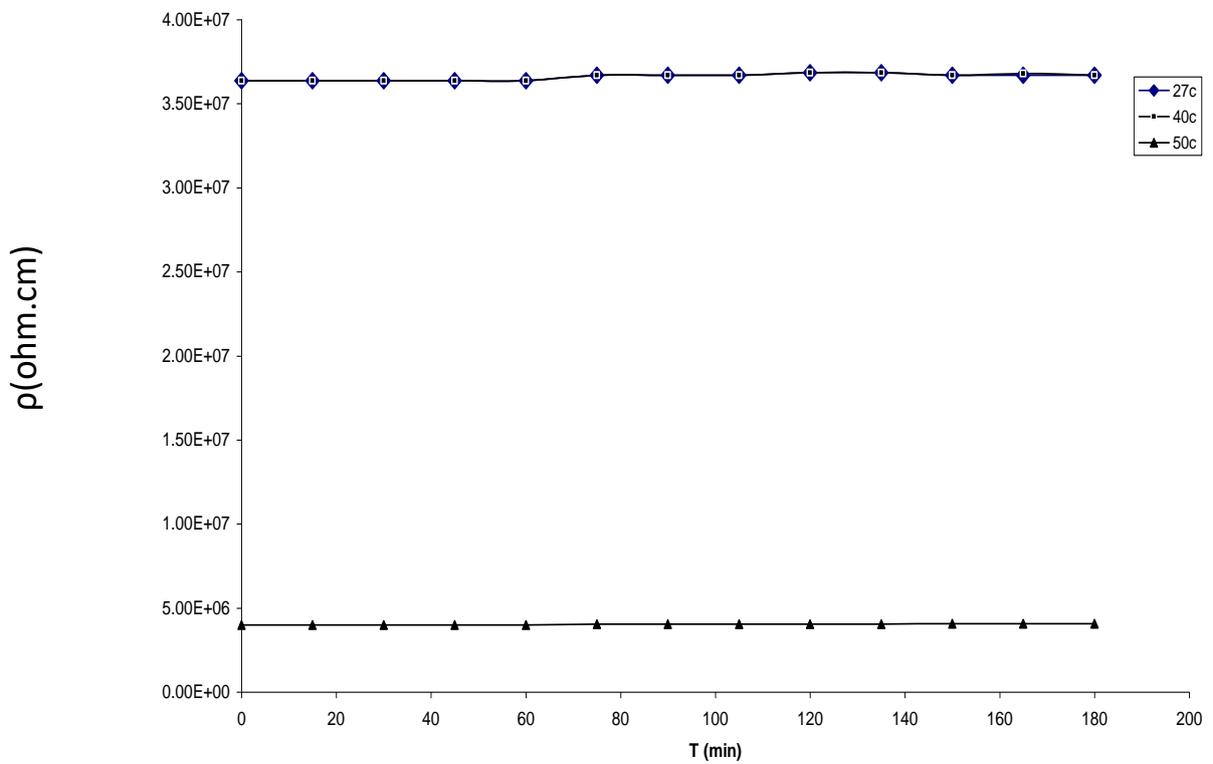


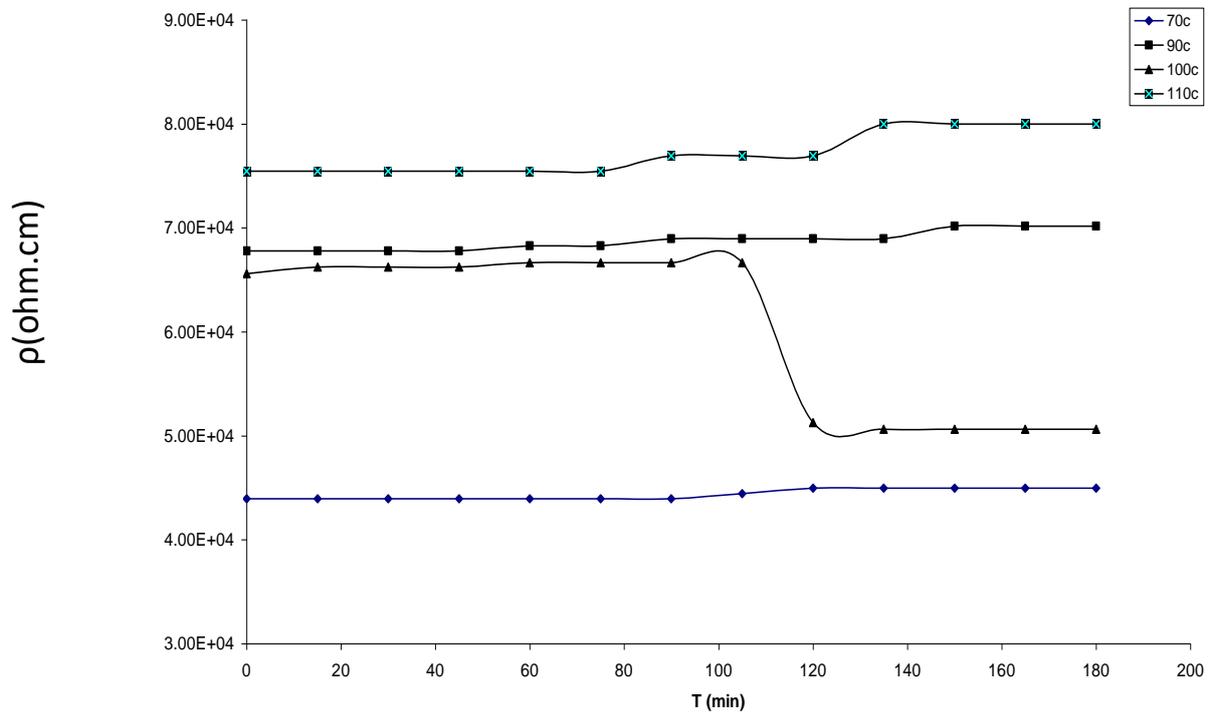
Fig(3-9): Relation ship between the resistivity with the time in different temperature of (L₁,PDCrG₁)polymer



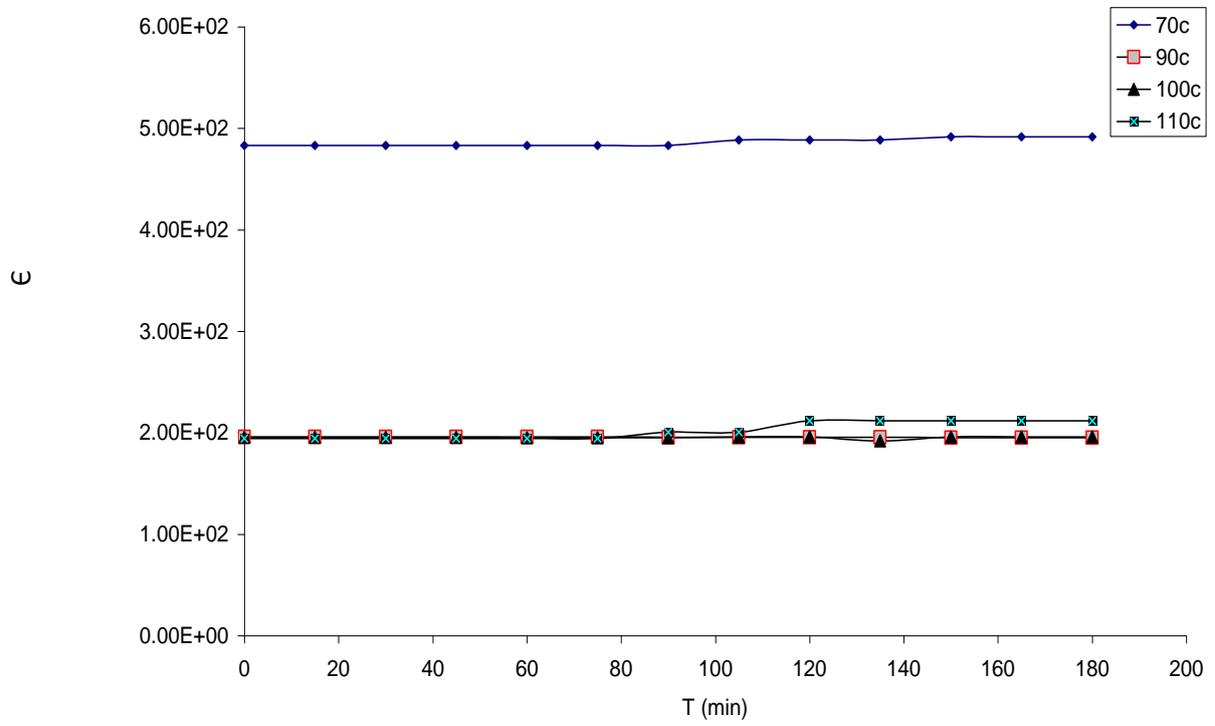
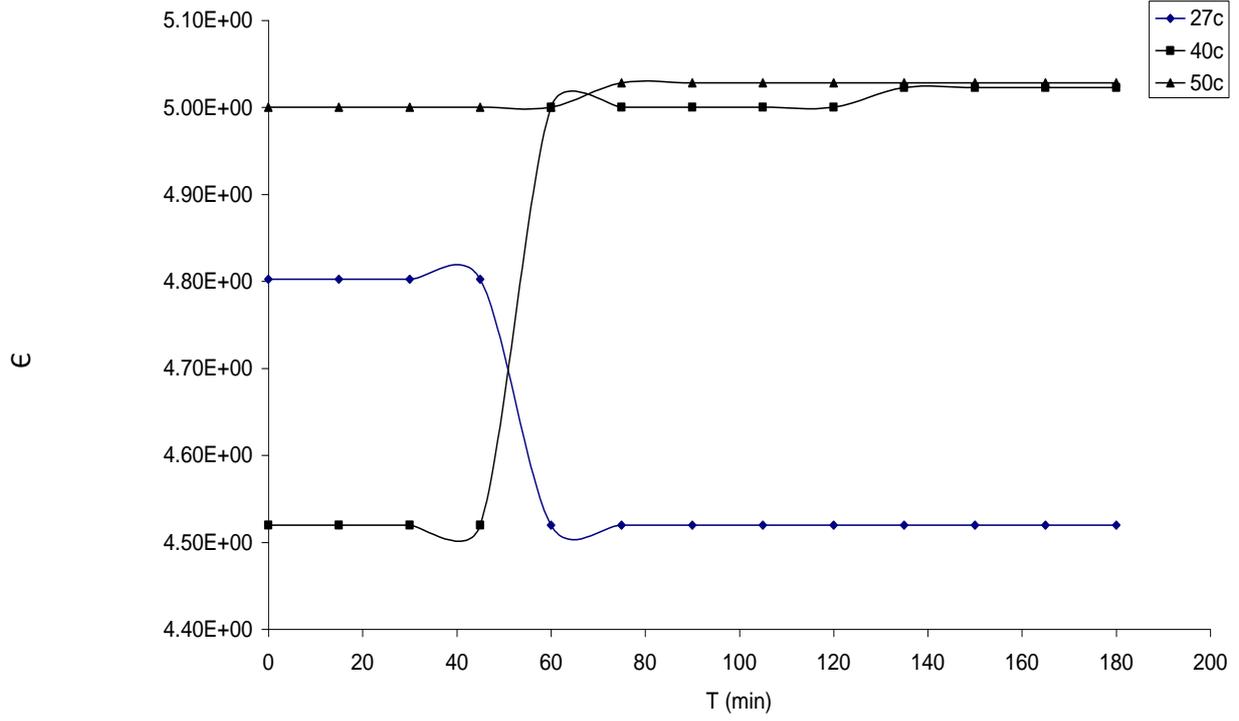


Fig(۳-۱۰): Relation ship between the permittivity with the time in different temperature of (L_{1,4}PDCrG₁)polymer

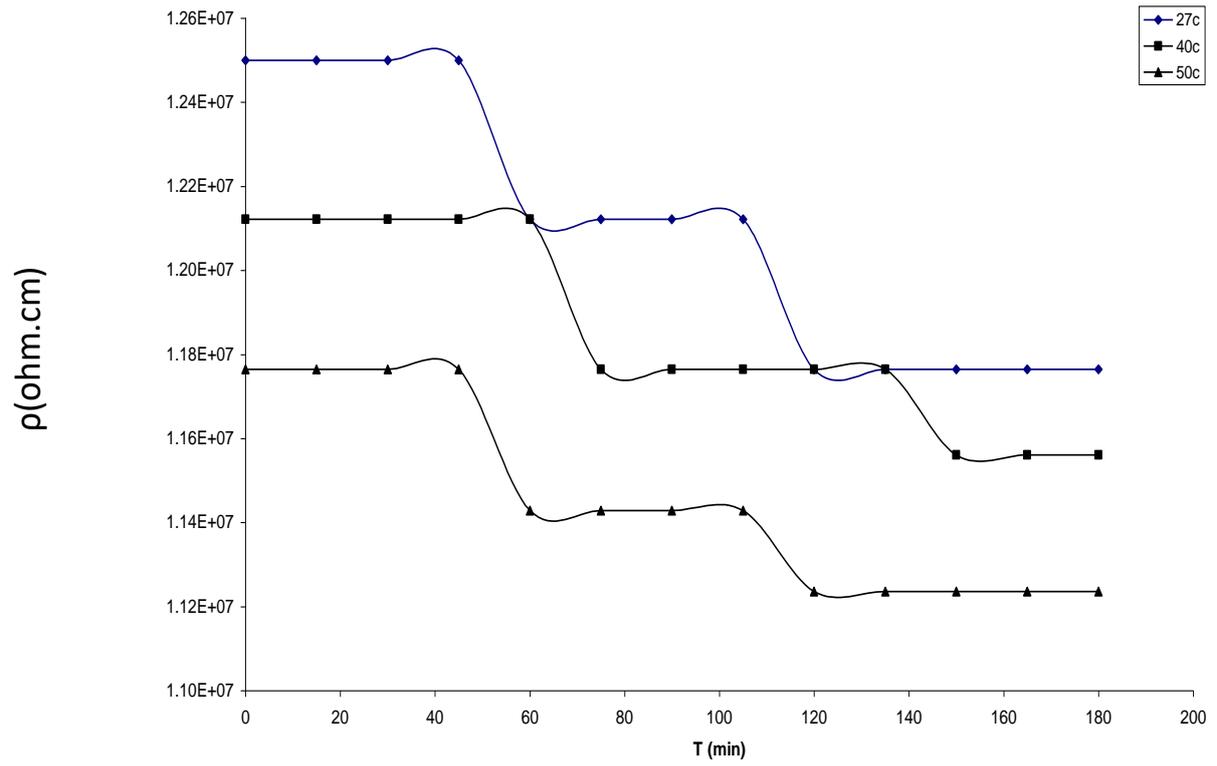


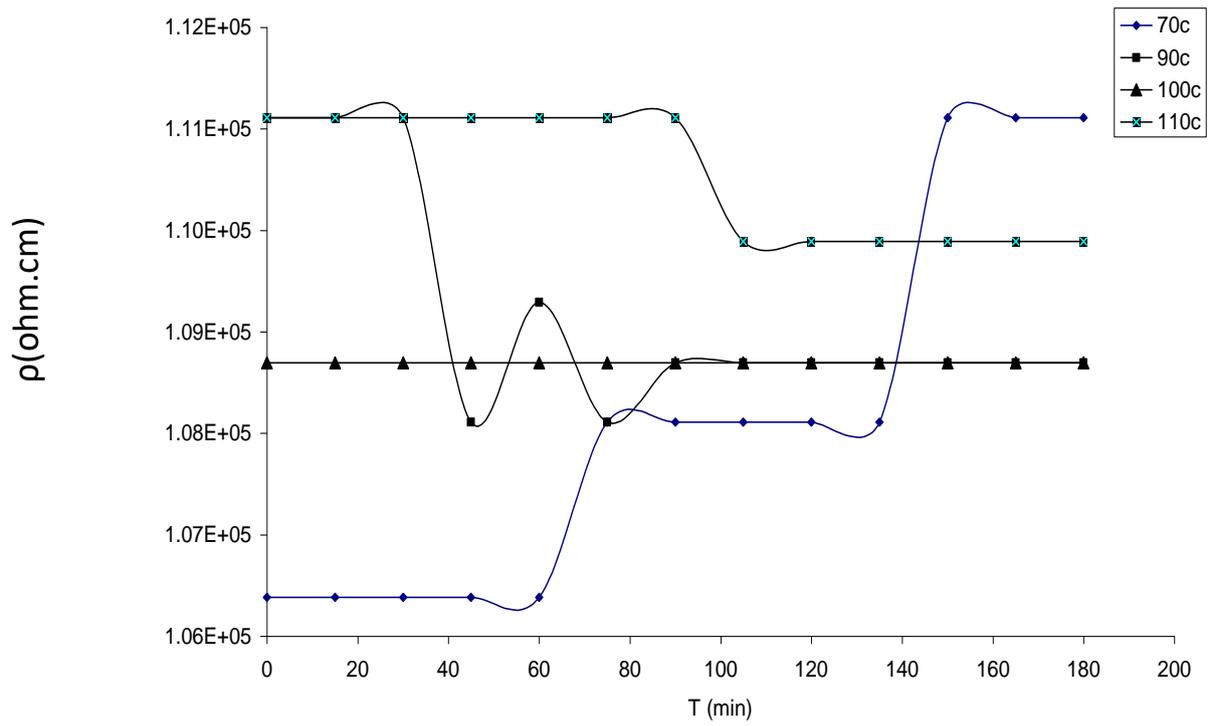


Fig(۳-۱۱): Relationship between the resistivity with the time in different temperature of (L_{1.4}PDCrG₁)polymer

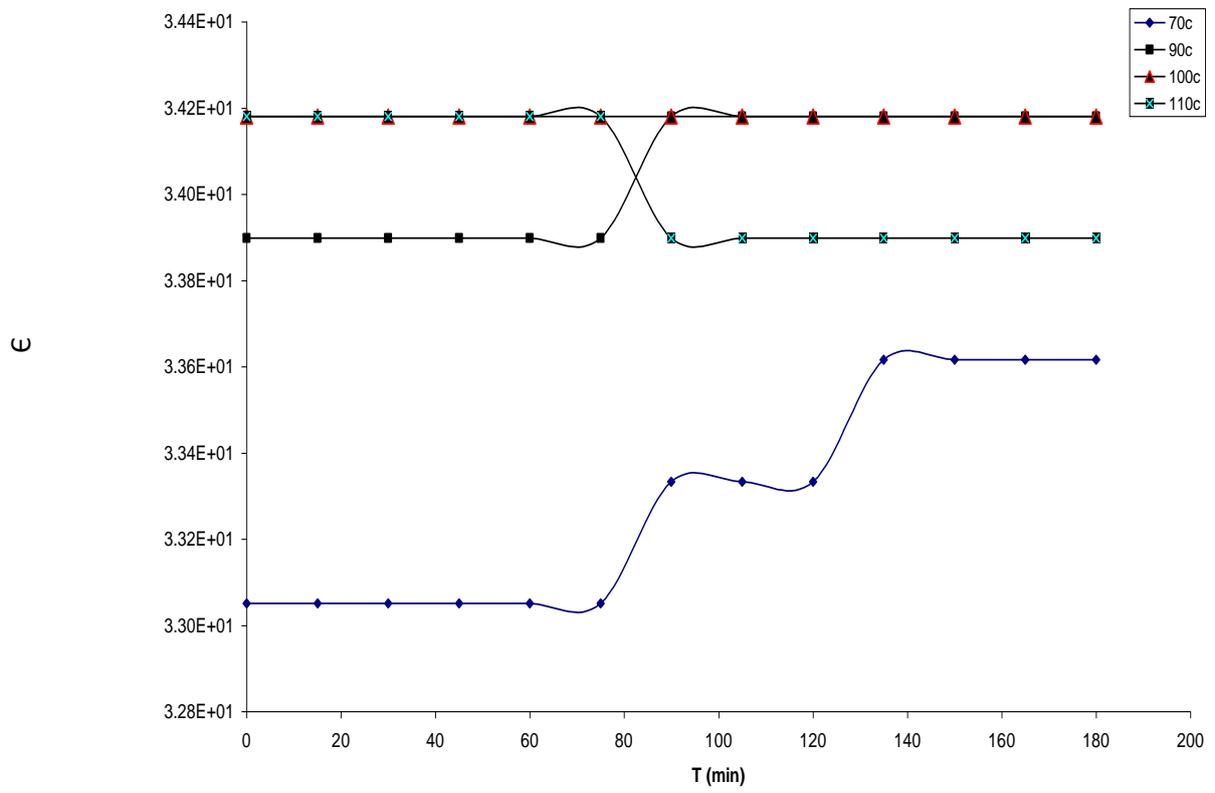
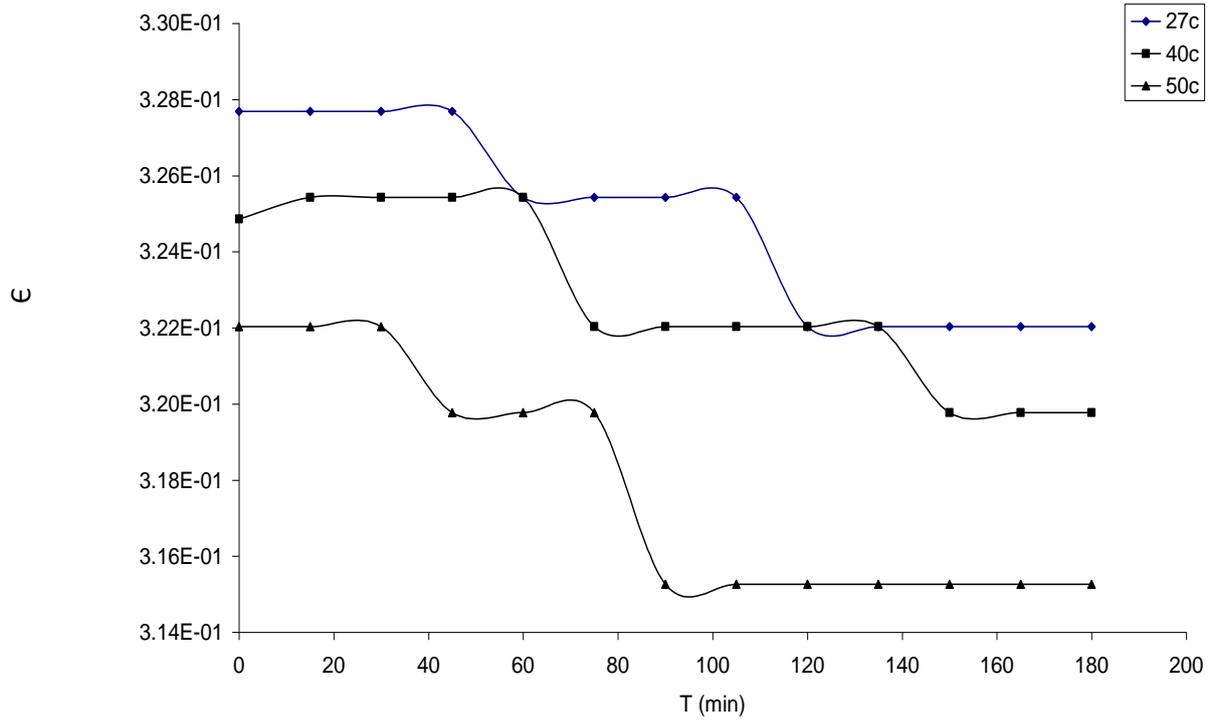


Fig(۳-۱۲): Relationship between the permittivity with the time in different temperature of (L_۱,PDCrG_۱)polymer

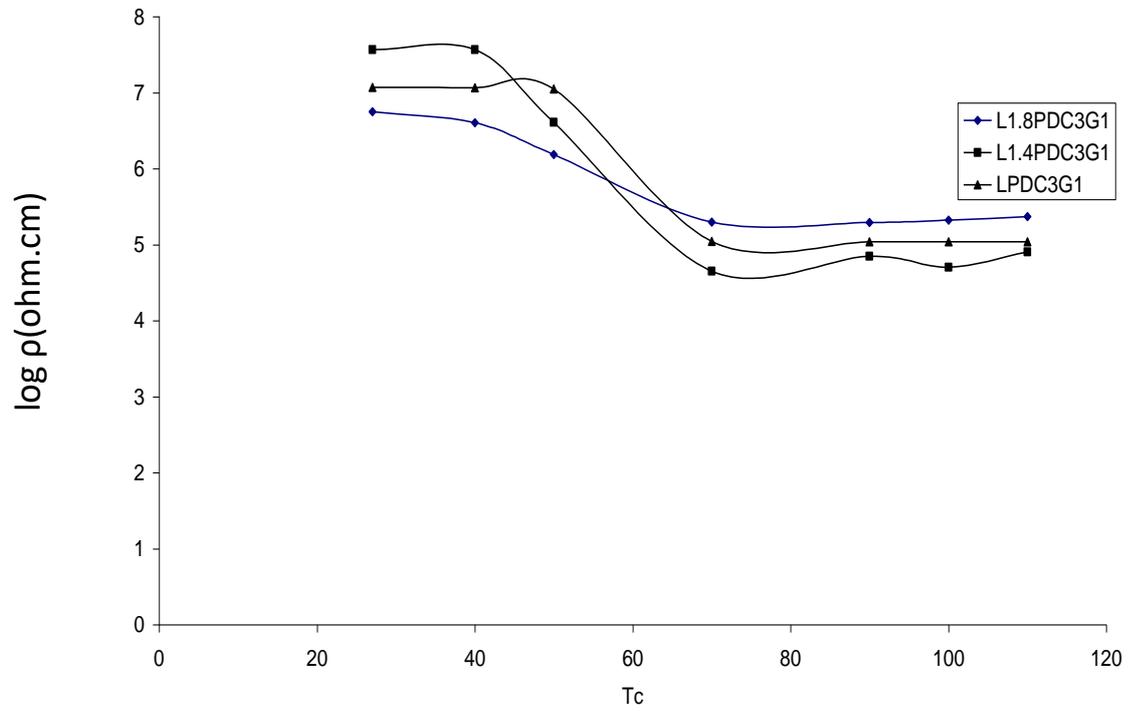




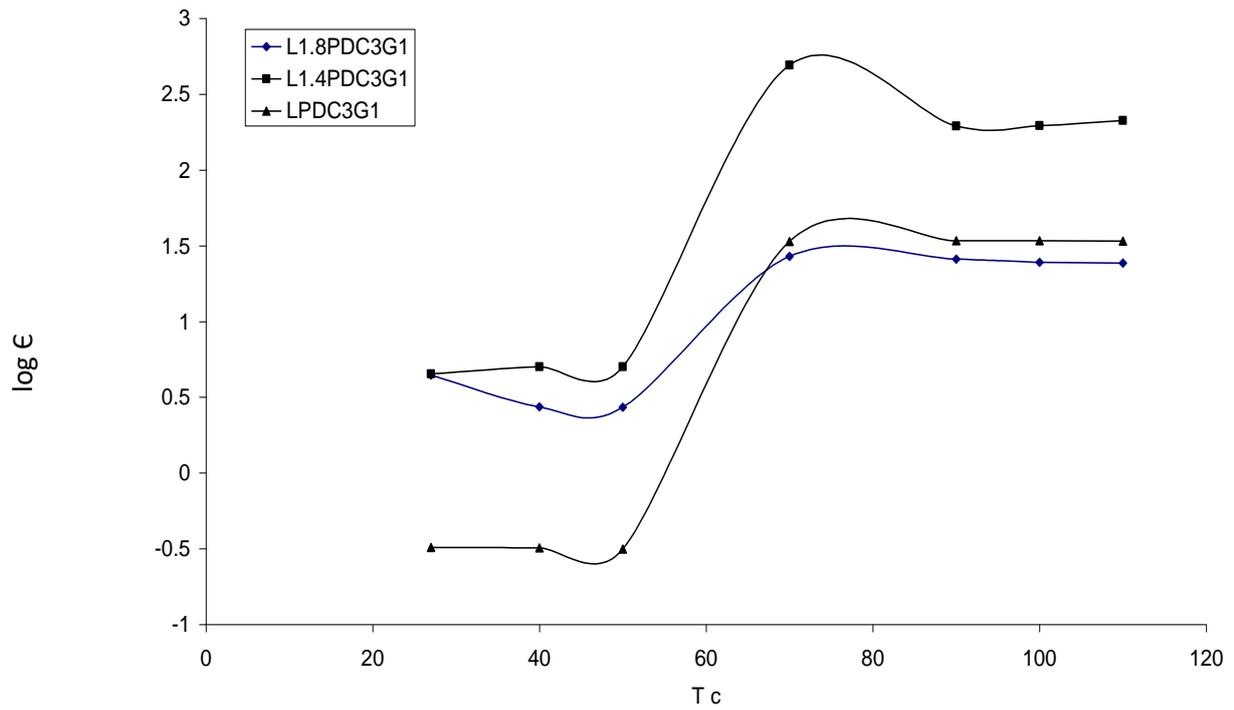
Fig(۳-۱۳): Relationship between the resistivity with the time in different temperature of (LPDCrG) polymer



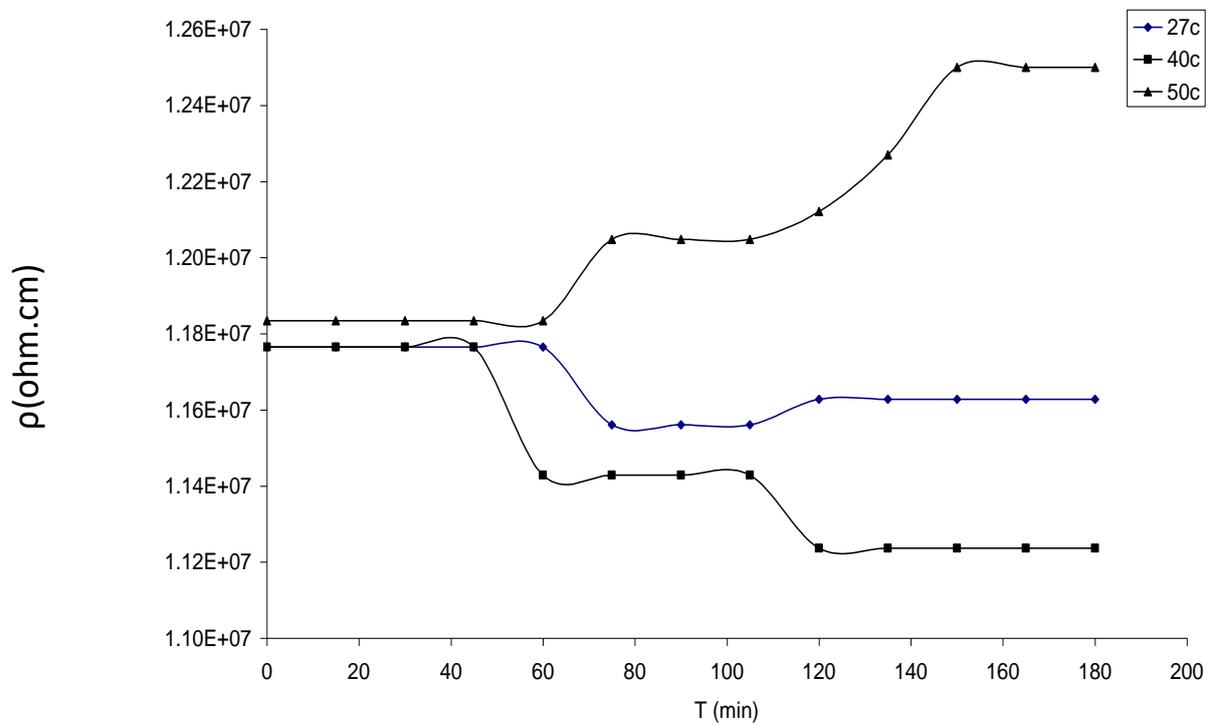
Fig(3-14): Relationship between the permittivity with the time in different temperature of (LPDCrG₁)polymer

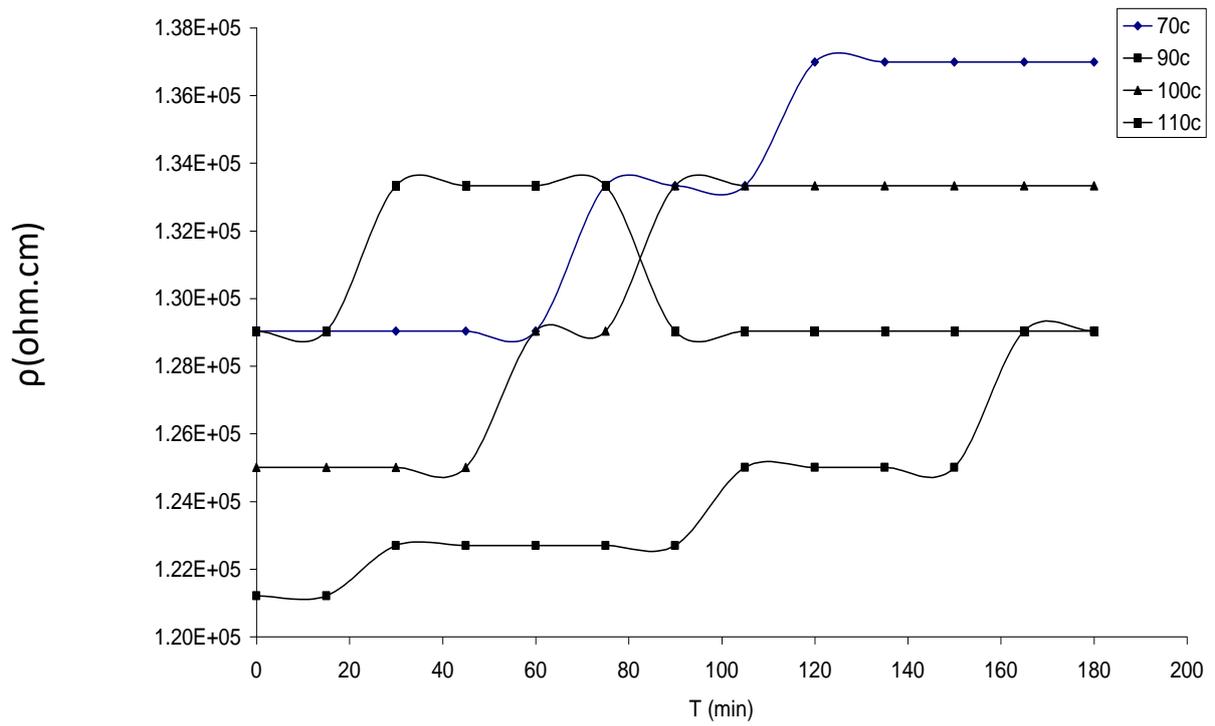


Fig(3-15): Relationship between the resistivity with the temperature for (L_{1.8}PDCrG₁, L_{1.4}PDCrG₁,LPDCrG₁)polymers

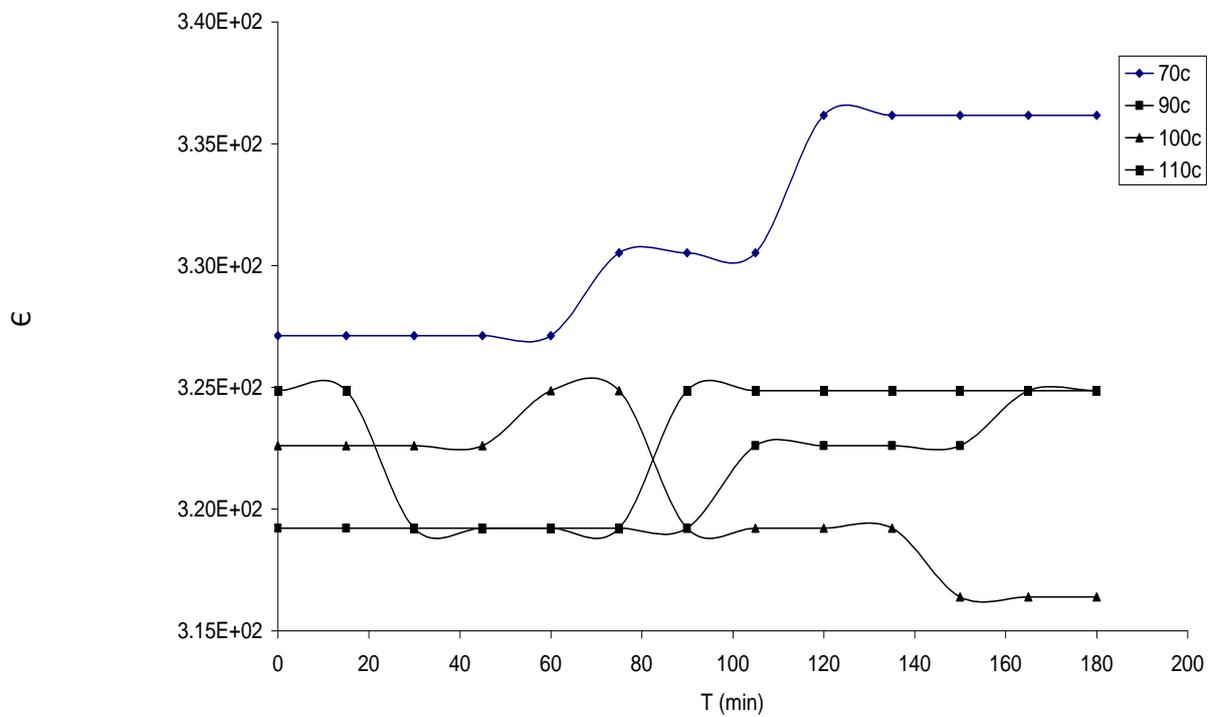
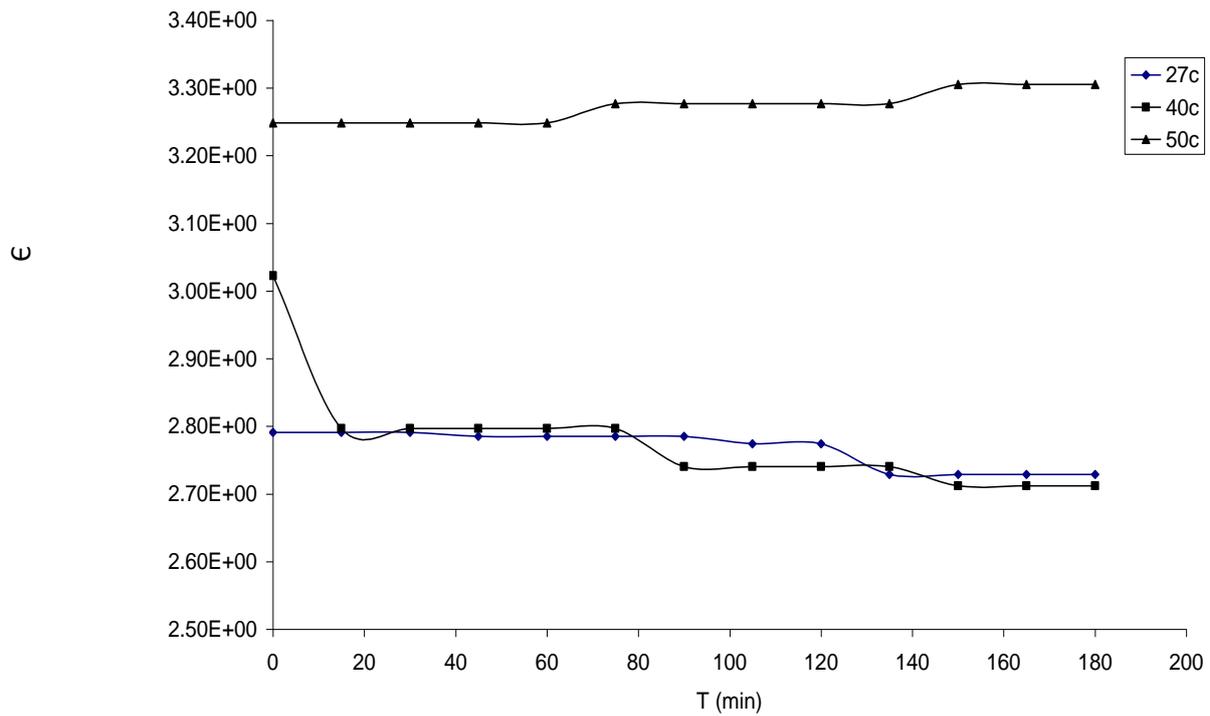


Fig(3-16): Relationship between the permittivity with the temperature for (L_{1.8}PDCrG₁, L_{1.4}PDCrG₁,LPDCrG₁) polymers

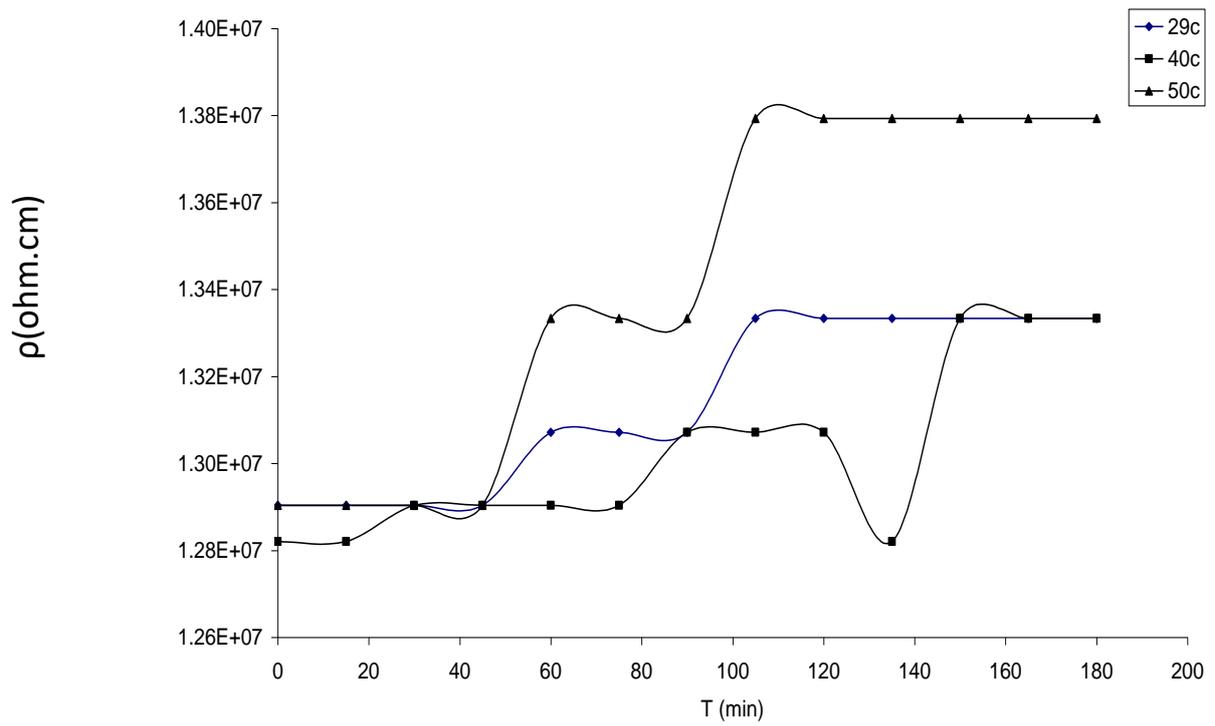


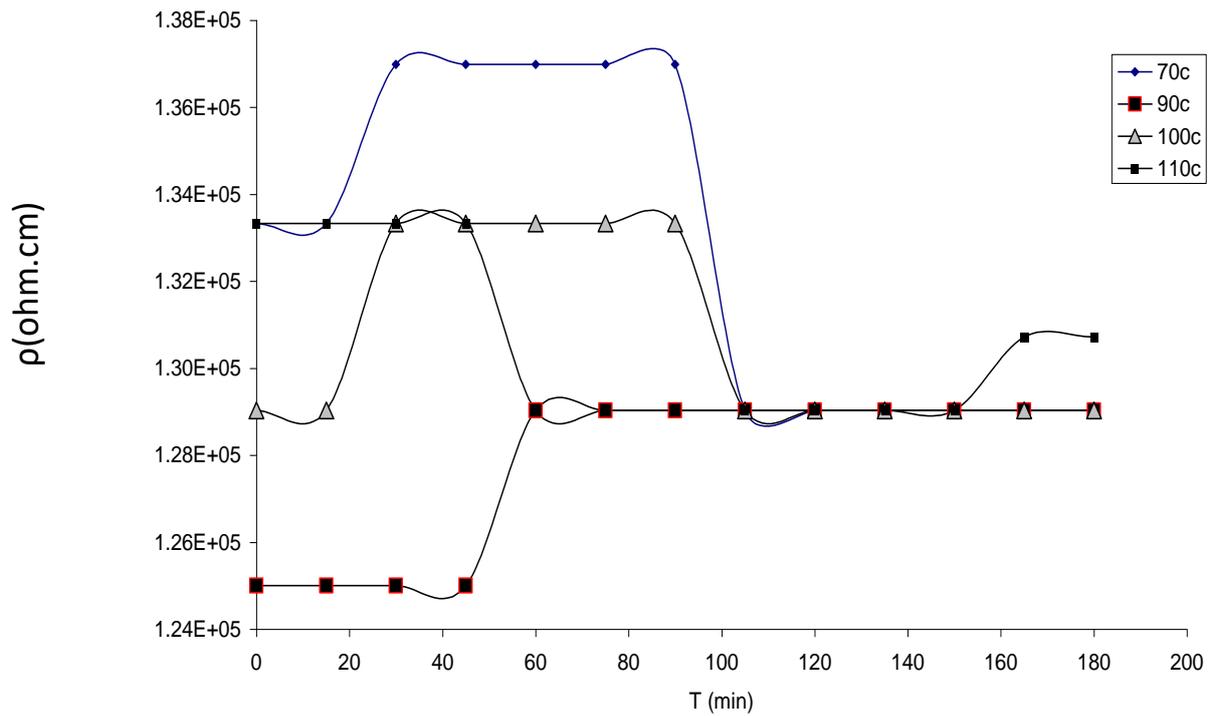


Fig(3-17): Relationship between the resistivity with the time in different temperature of (L,Δ)PDCG polymer

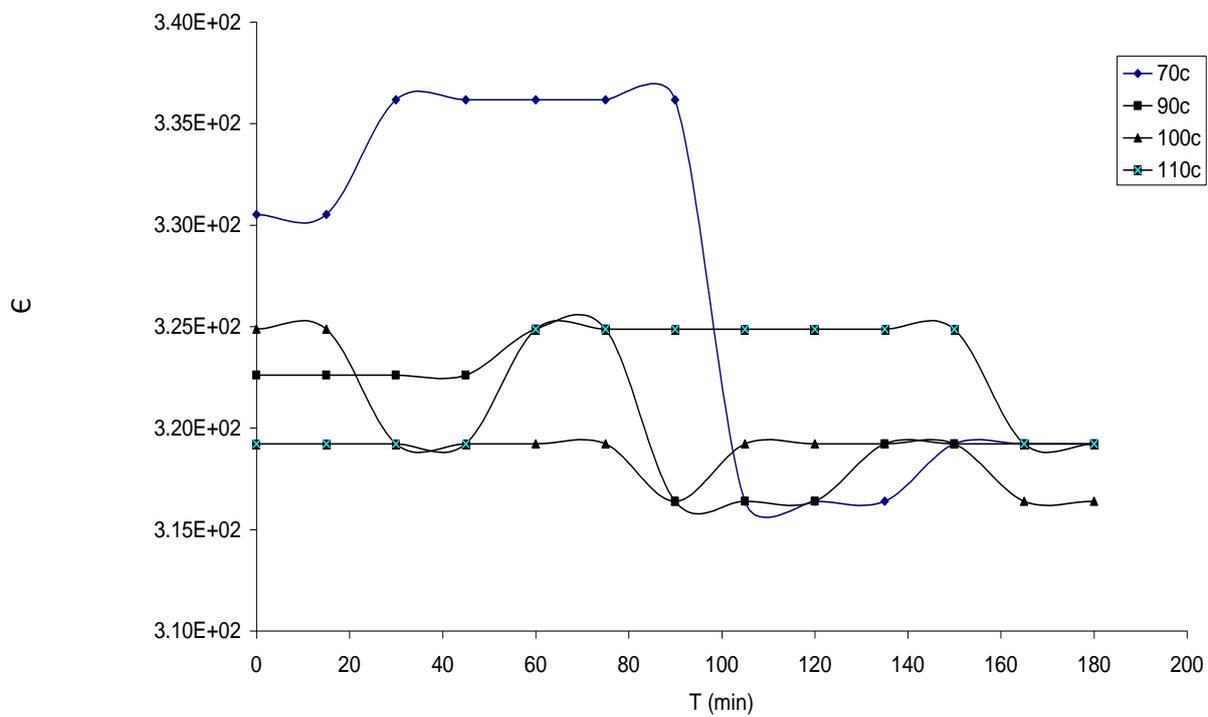
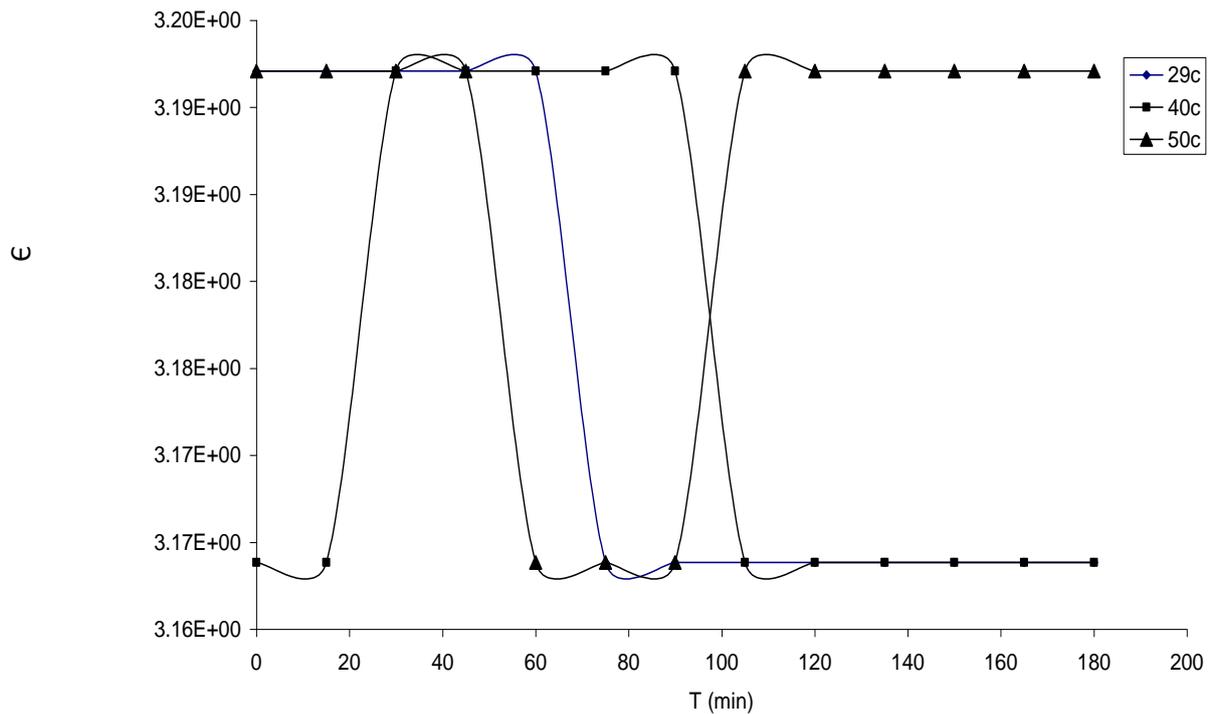


Fig(3-11): Relation ship between the permittivity with the time in different temperature of (L₁,^ΔPDCG)polymer

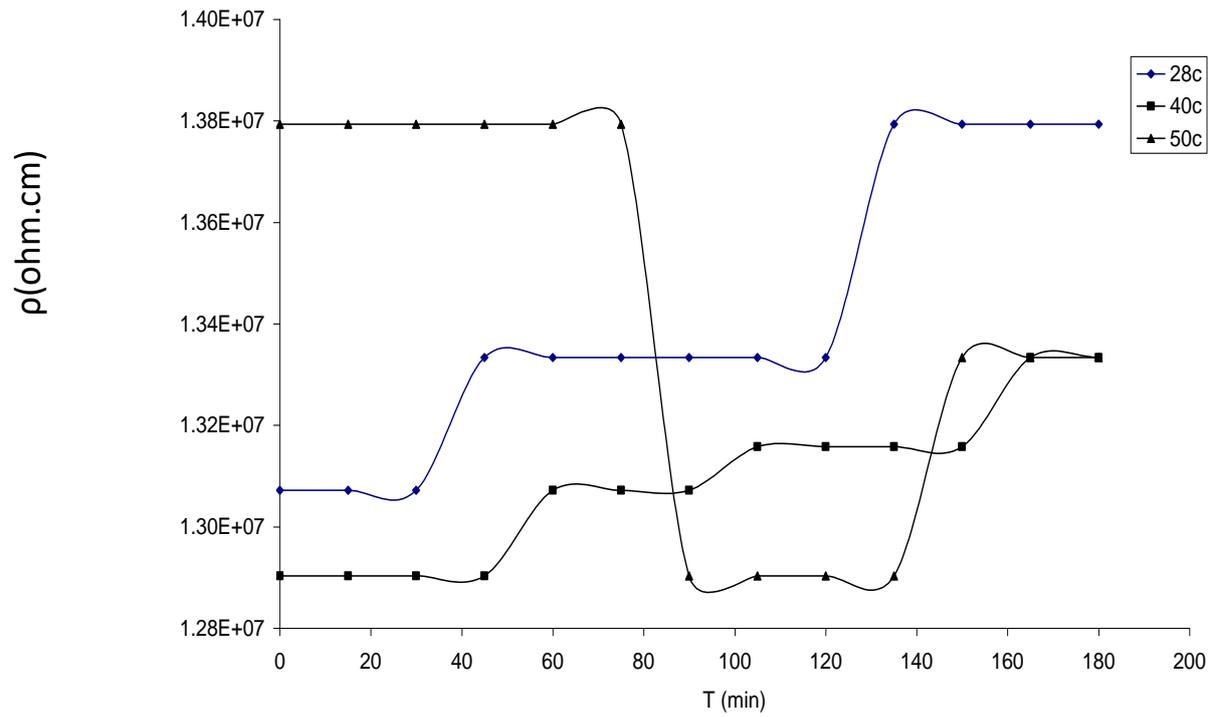


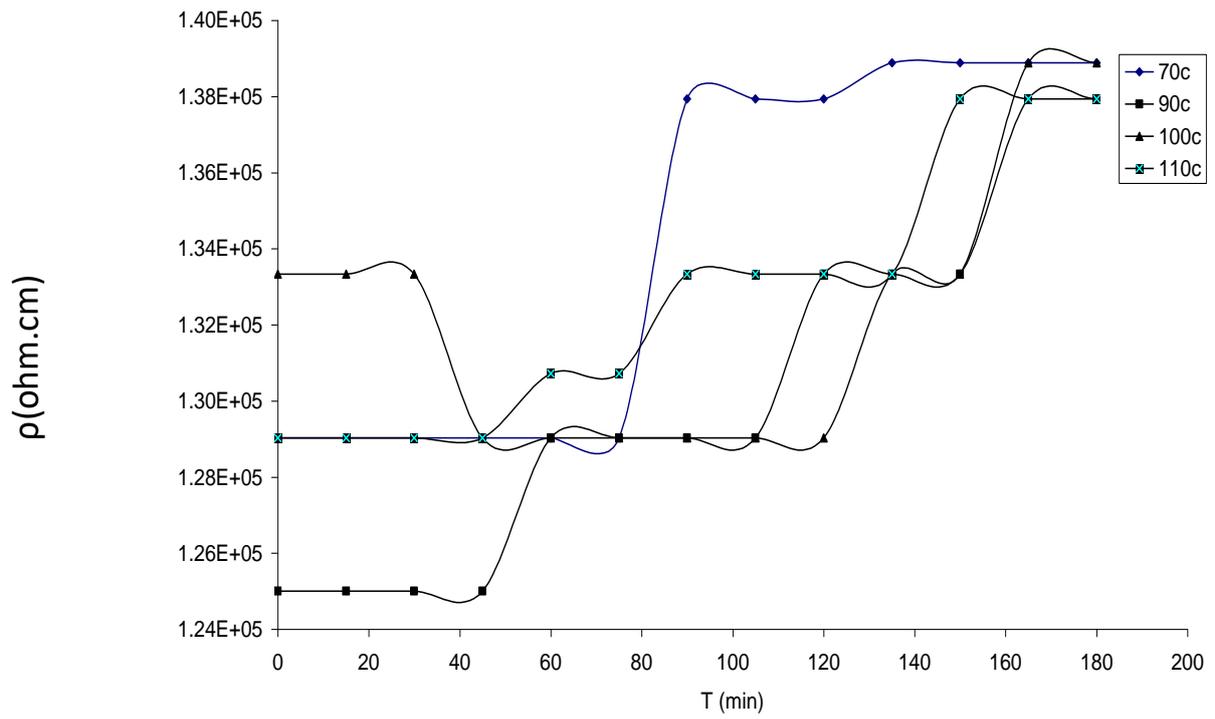


Fig(۳-۱۹): Relationship between the resistivity with the time in different temperature of (L_{1,ε} PDCG)polymer

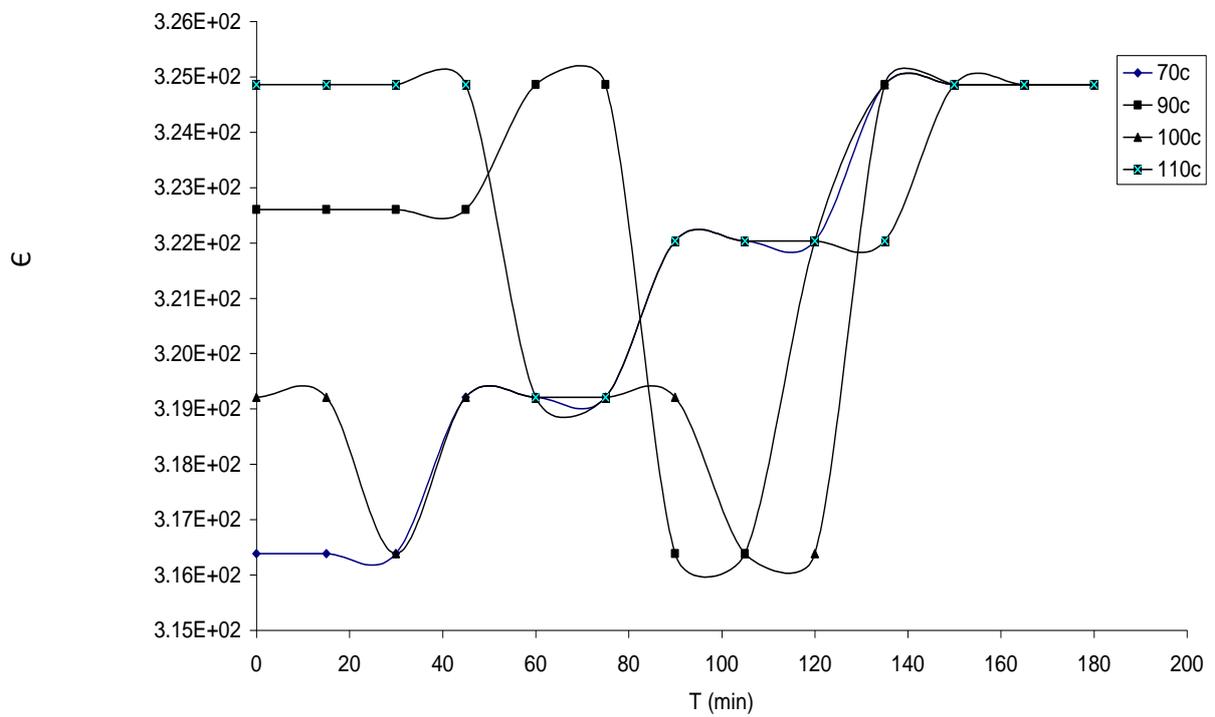
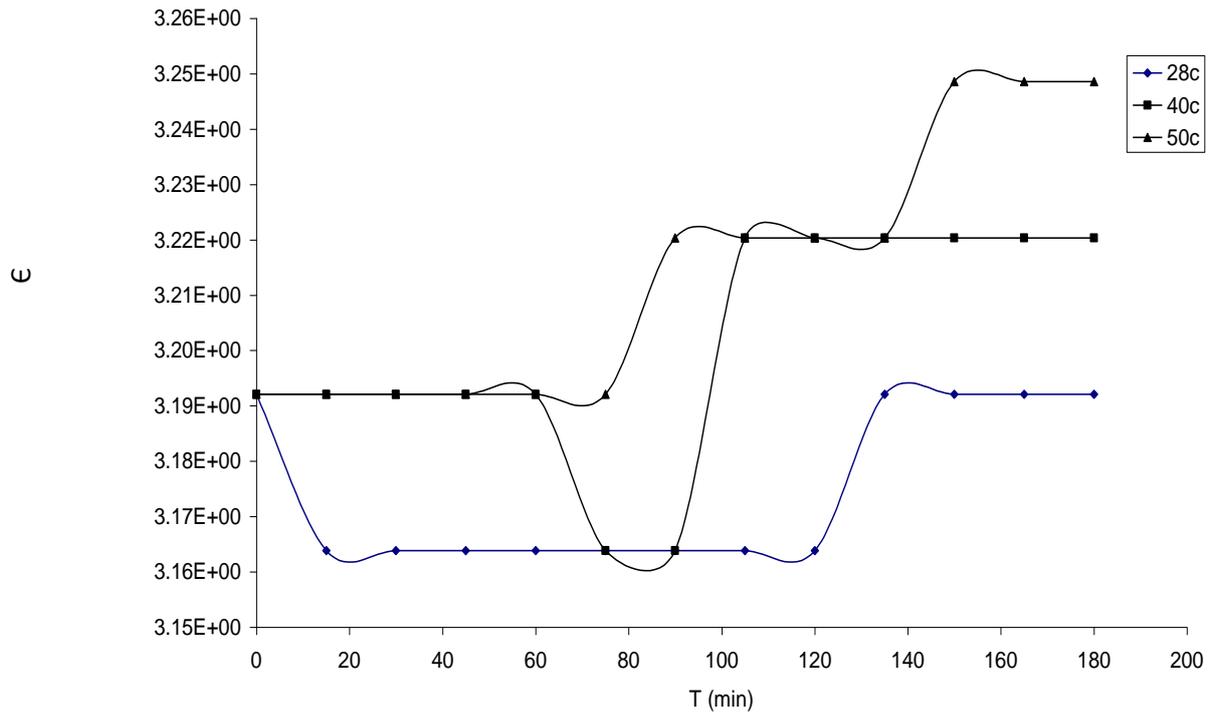


Fig(۳-۲۰): Relation ship between the permittivity with the time in different temperature of (L_{۱,۴}PDCG)polymer

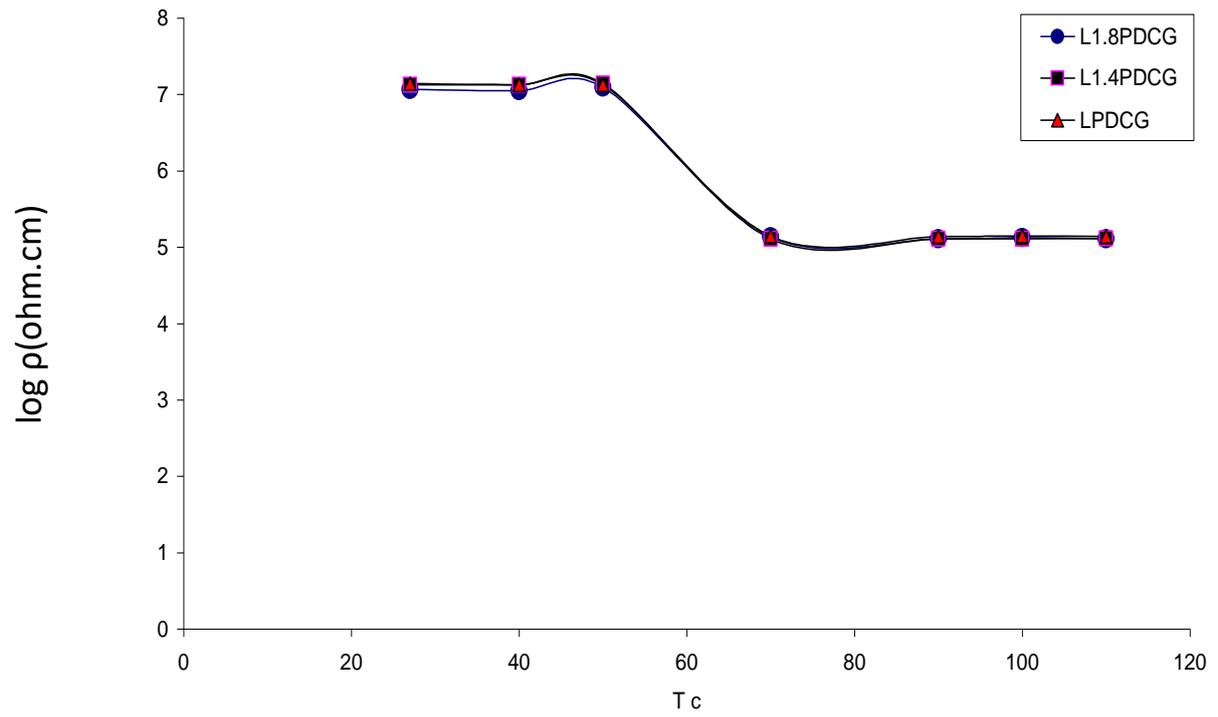




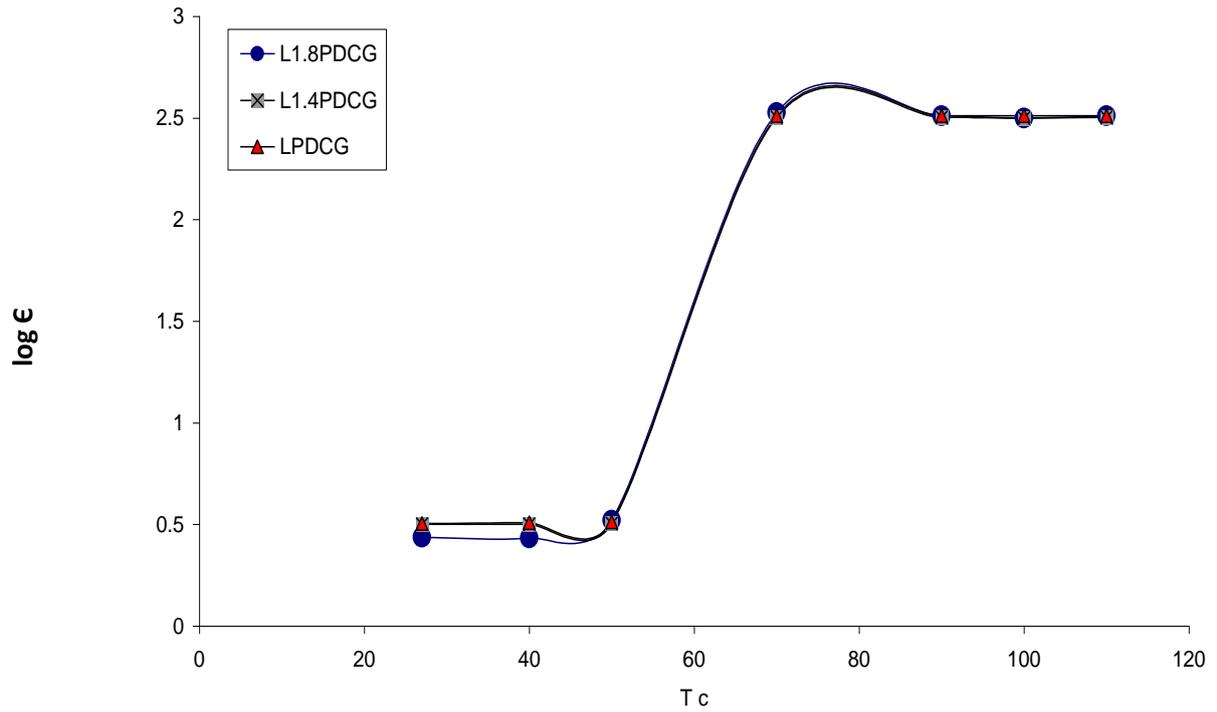
Fig(۳-۲۱): Relationship between the resistivity with the time in different temperature of (LPDCG)polymer



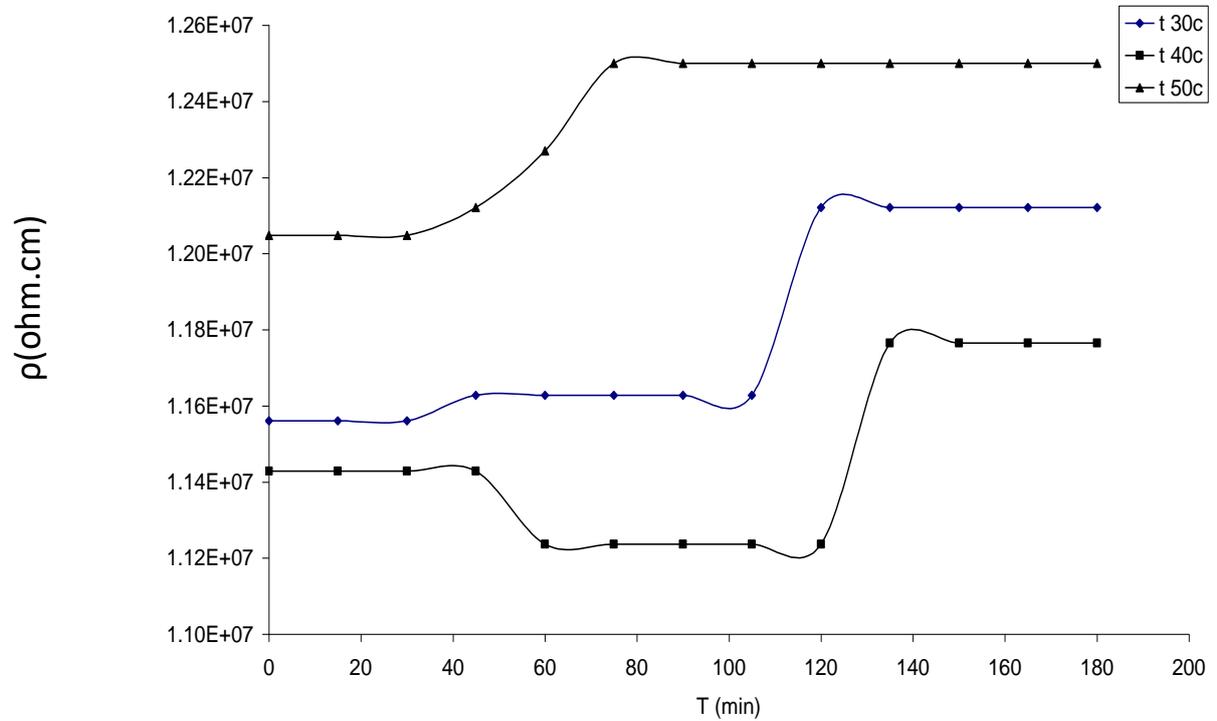
Fig(۳-۲۲): Relation ship between the permittivity with the time in different temperature of (LPDCG)polymer



Fig(3-23): Relationship between the resistivity with the temperature for (L_{1.8}PDCG , L_{1.4} PDCG,LPDCG)polymers



Fig(3-24): Relationship between the permittivity with the temperature for (L1.8PDCG, L1.4PDCG, LPDCG) polymers



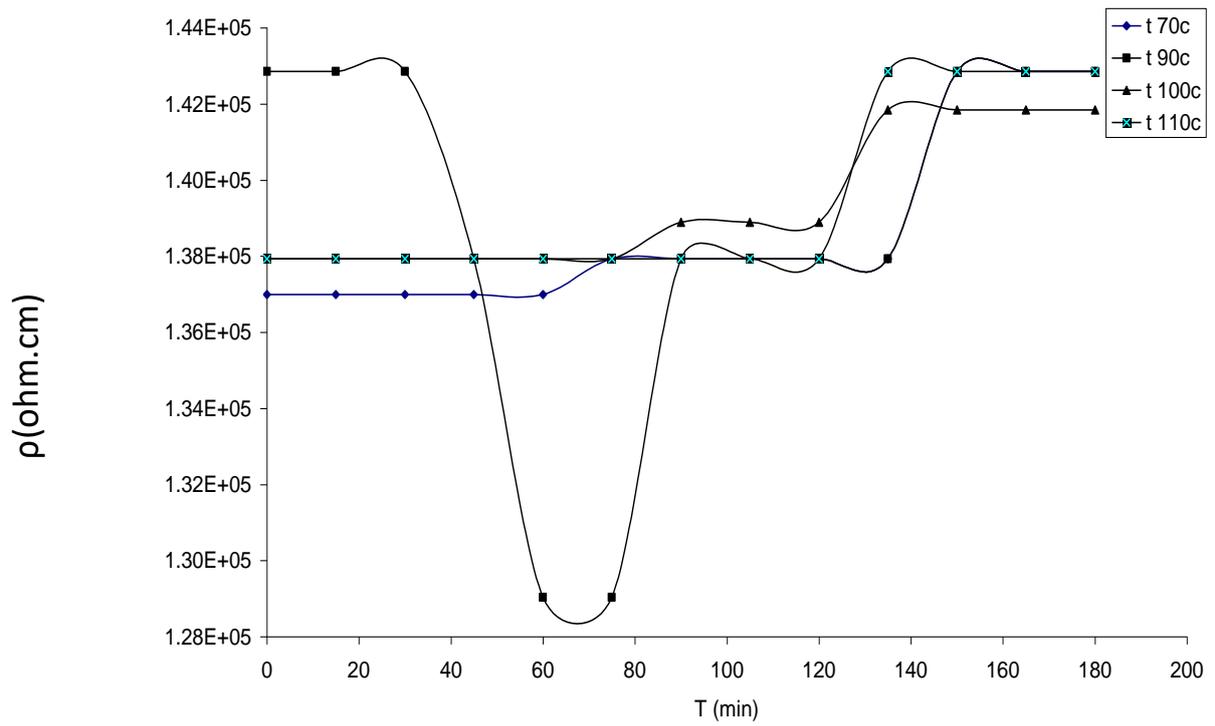


Fig.(۳-۲۰): Relation ship between the resistivity with the time in different temperature of (L,PDC,G)polymer

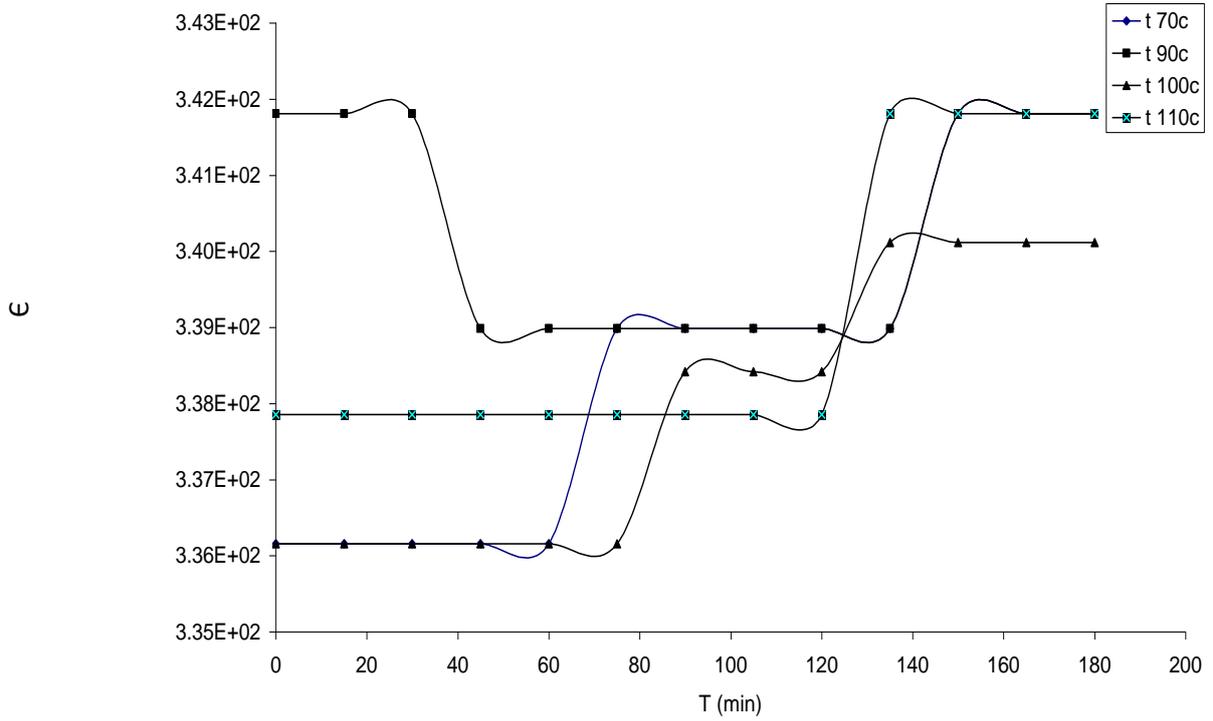
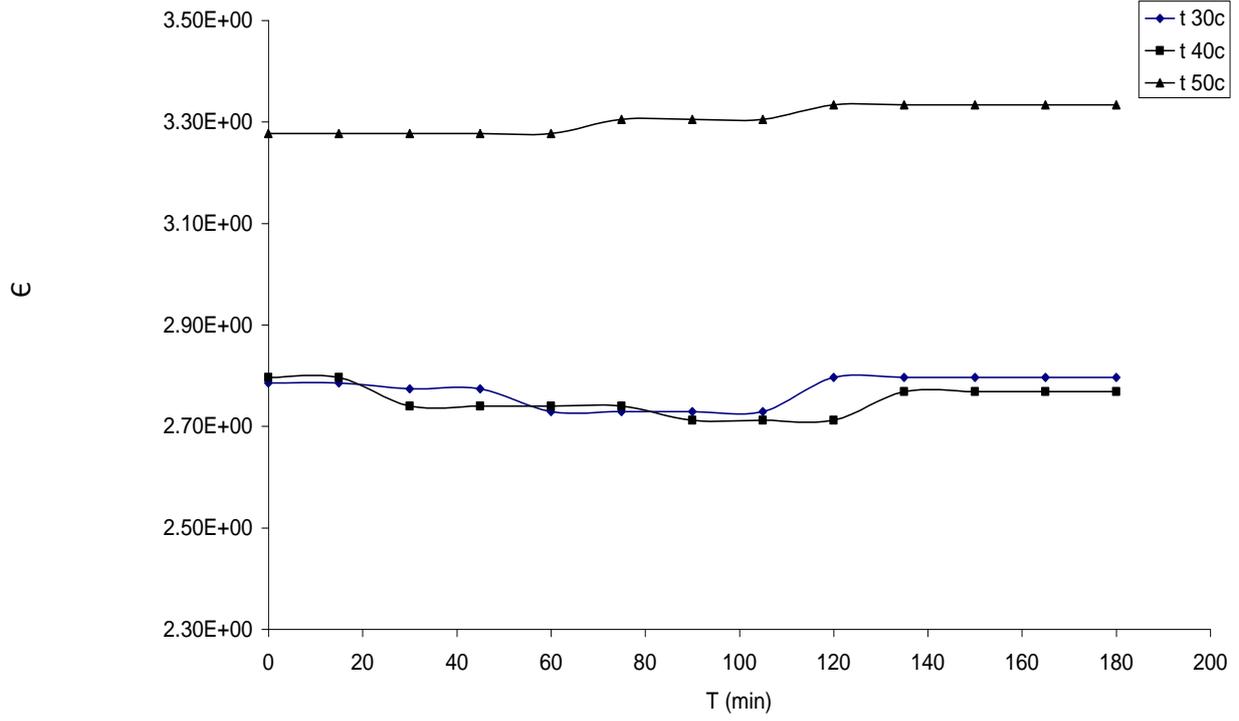
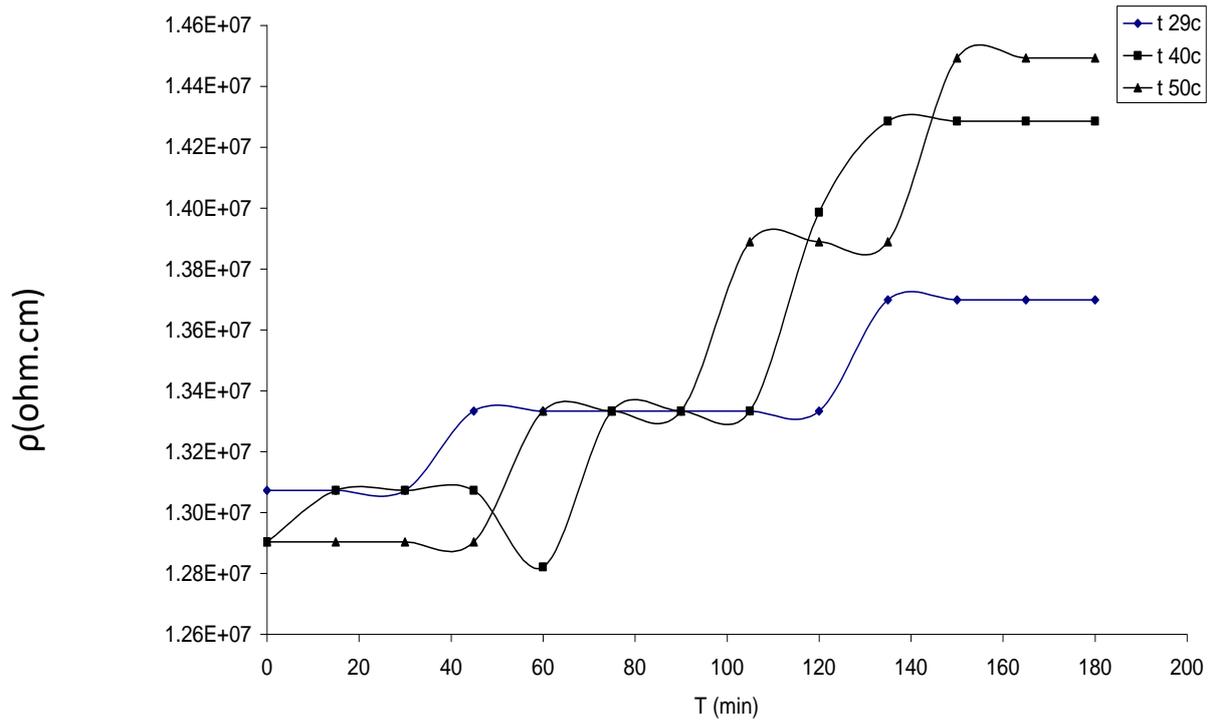


Fig.(۳-۲۶): Relationship between the permittivity with the time in different temperature of (L, PDC, Gr) polymer



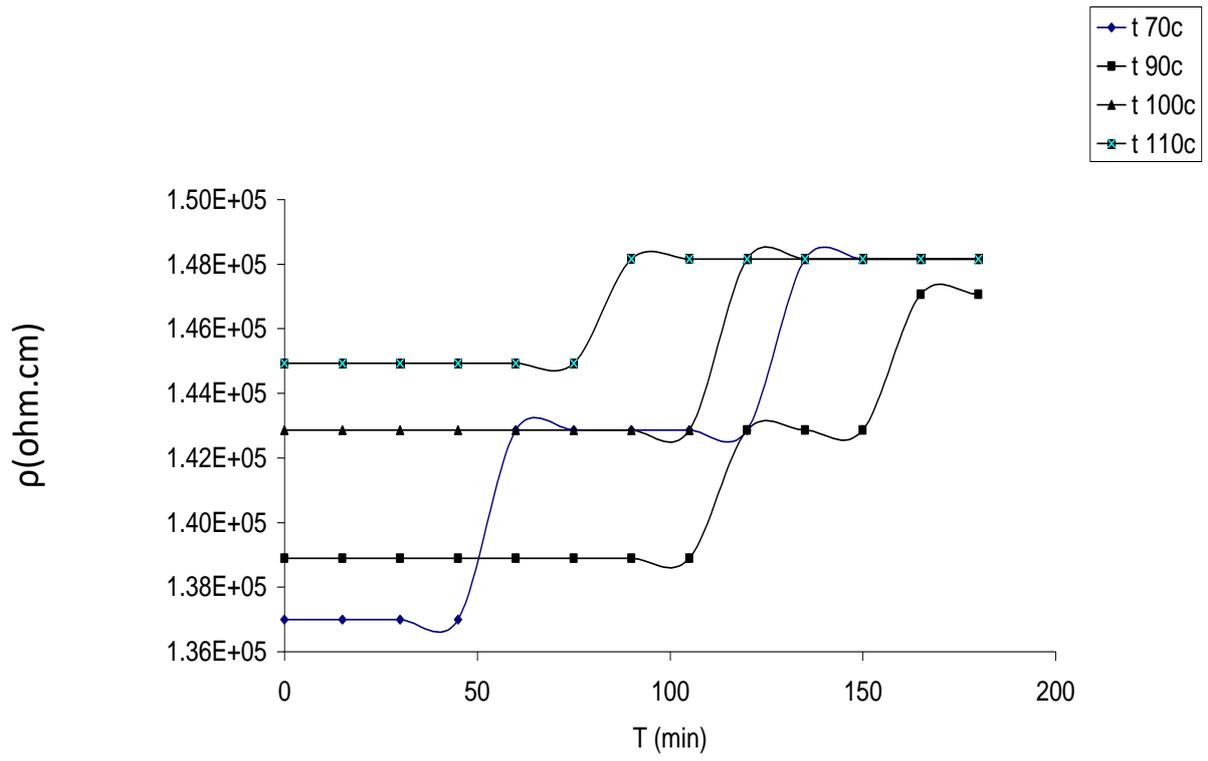


Fig.(3-27): Relationship between the resistivity with the time in different temperature of (LPDC, Gr) polymer

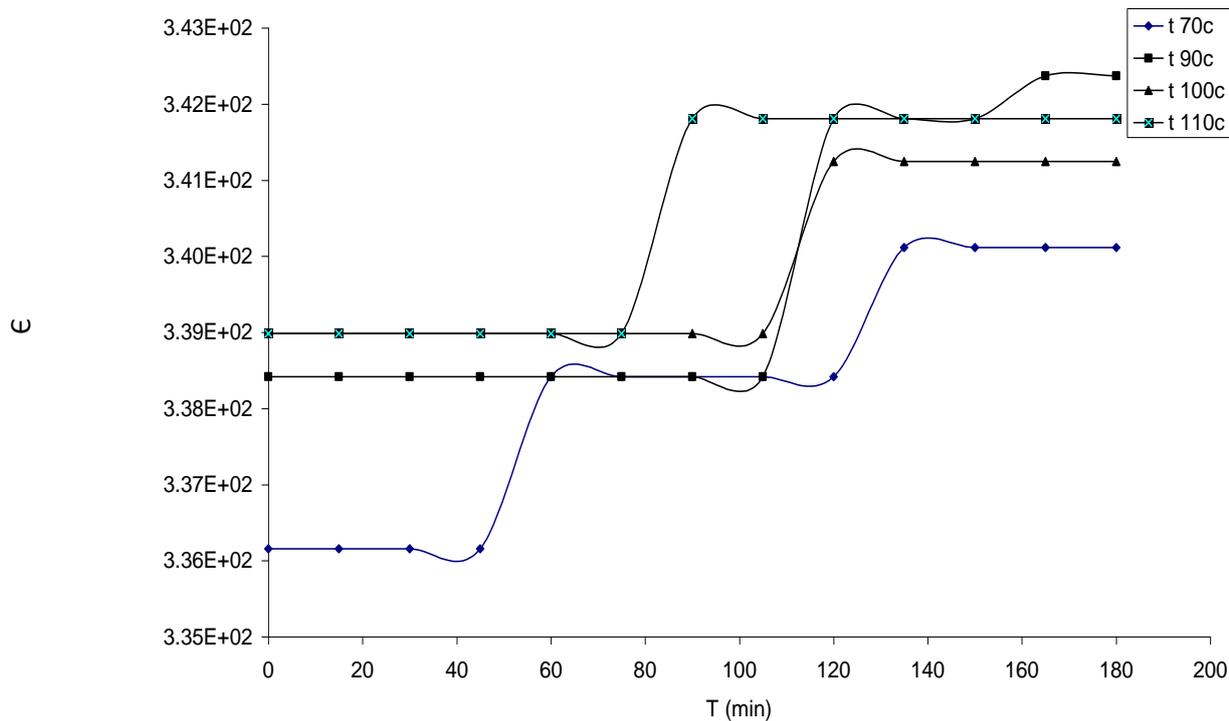
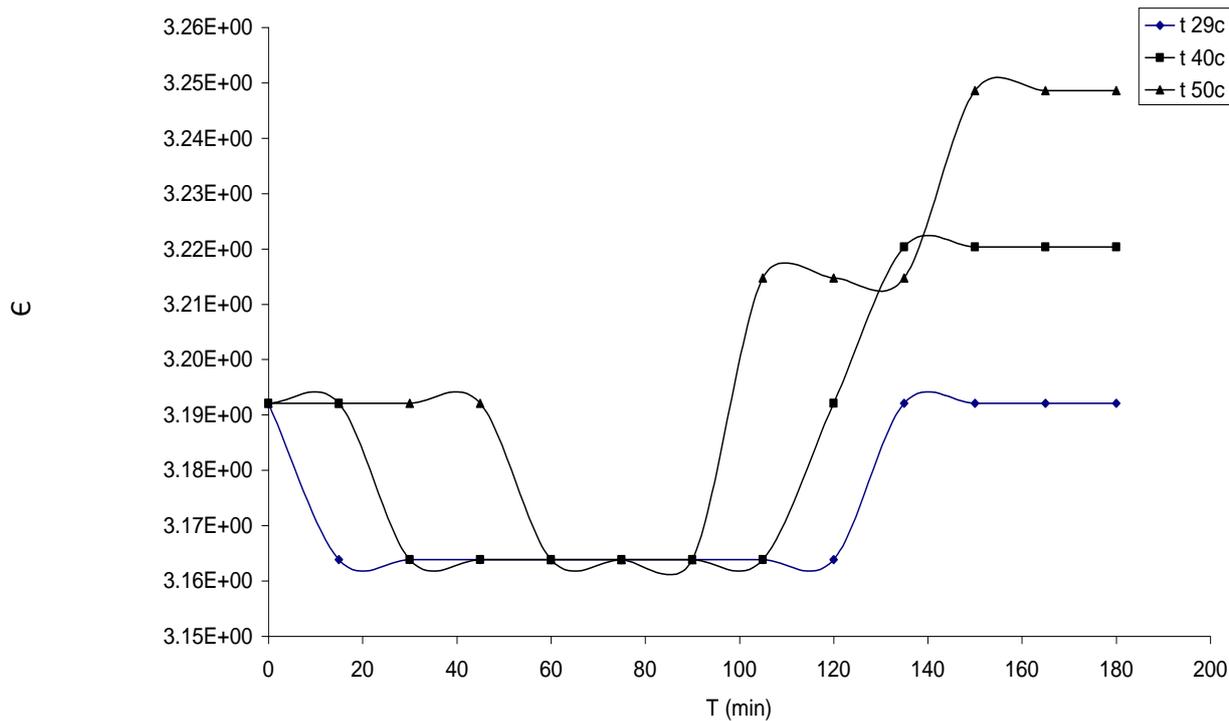
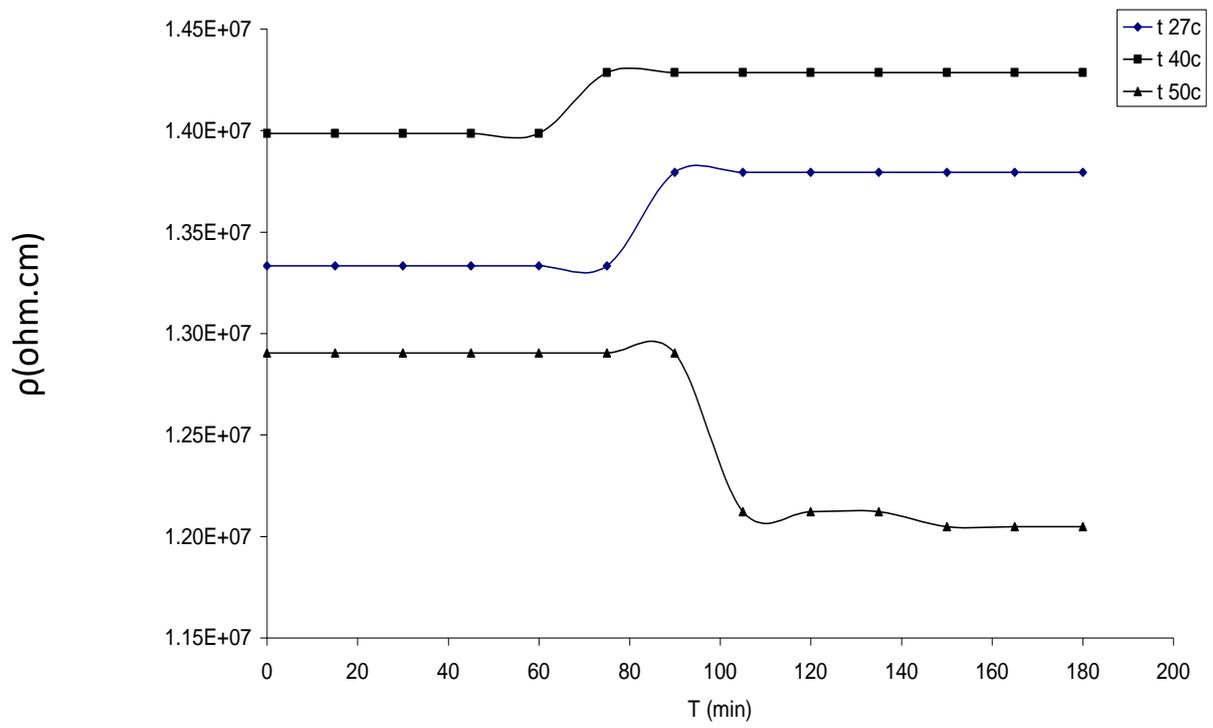


Fig.(۳-۲۸): Relation ship between the permittivity with the time in different temperature of (LPDC, Gr) polymer



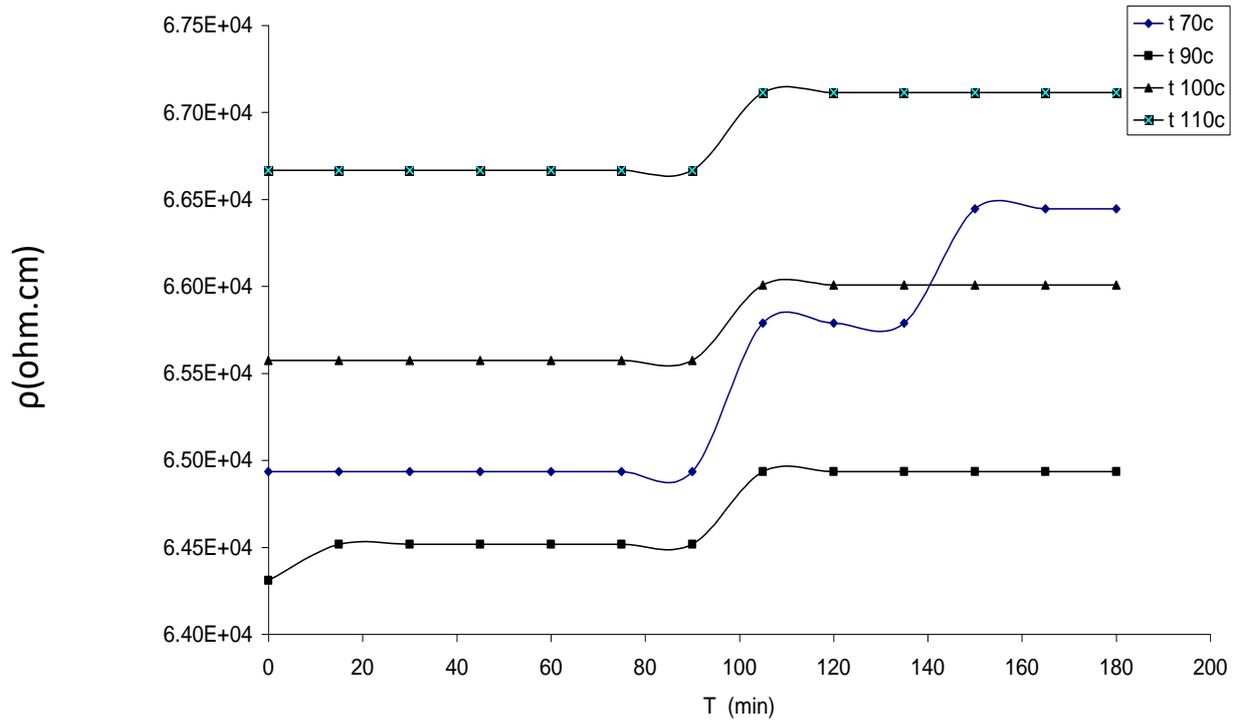


Fig.(۳-۲۹): Relationship between the resistivity with the time in different temperature of (LPDG)polymer

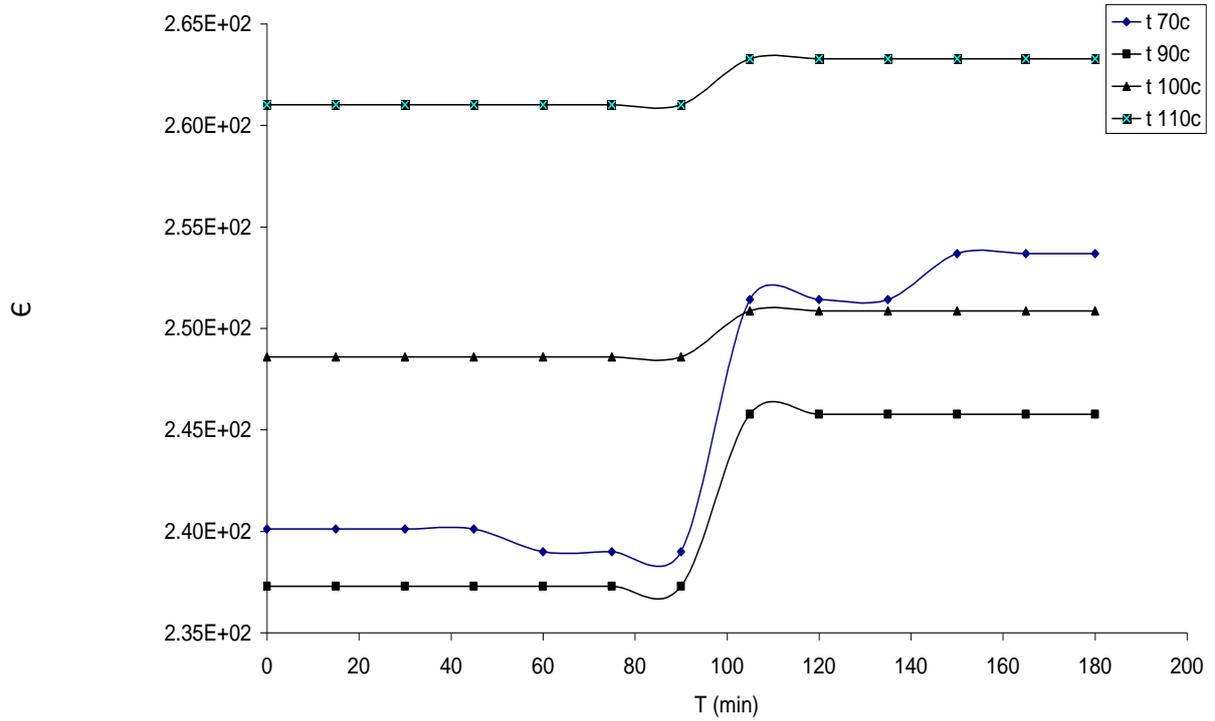
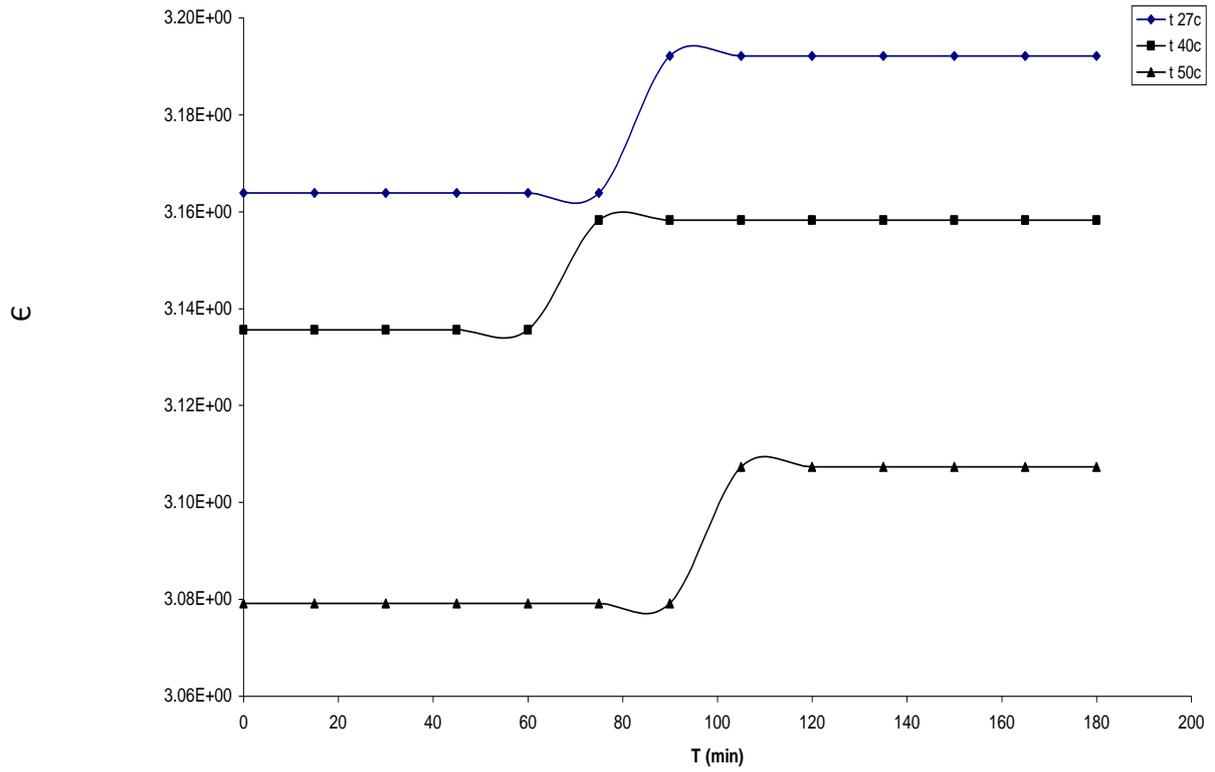
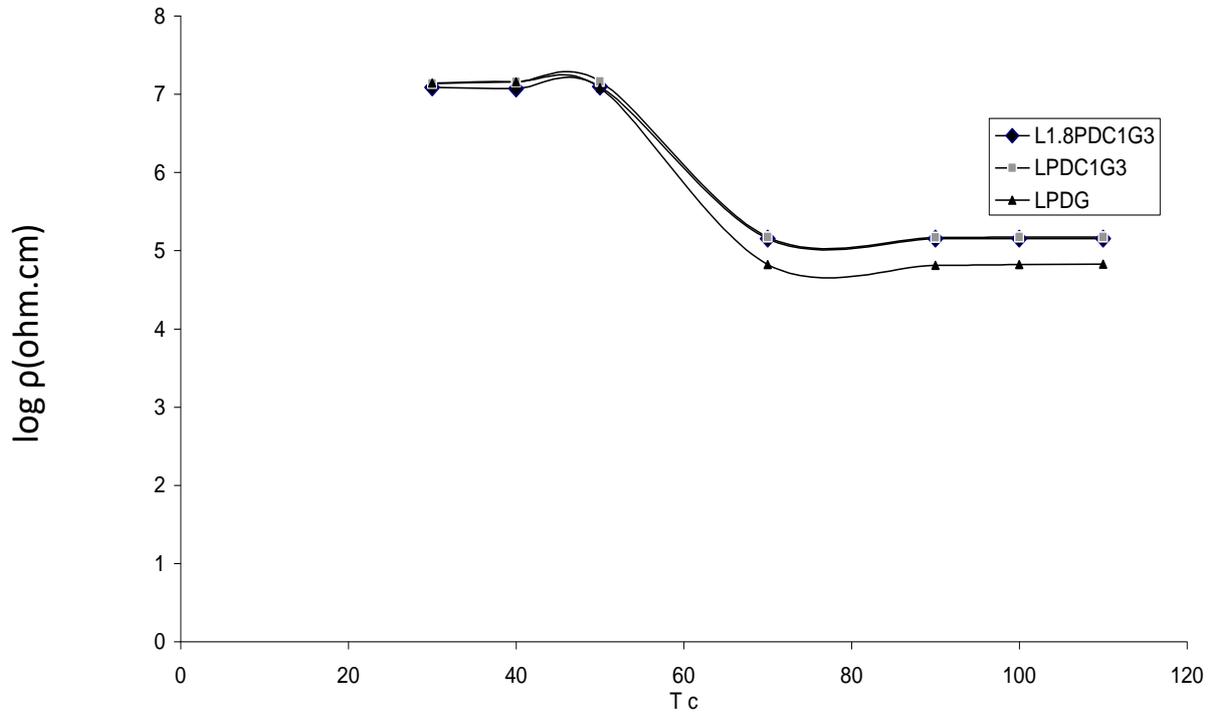
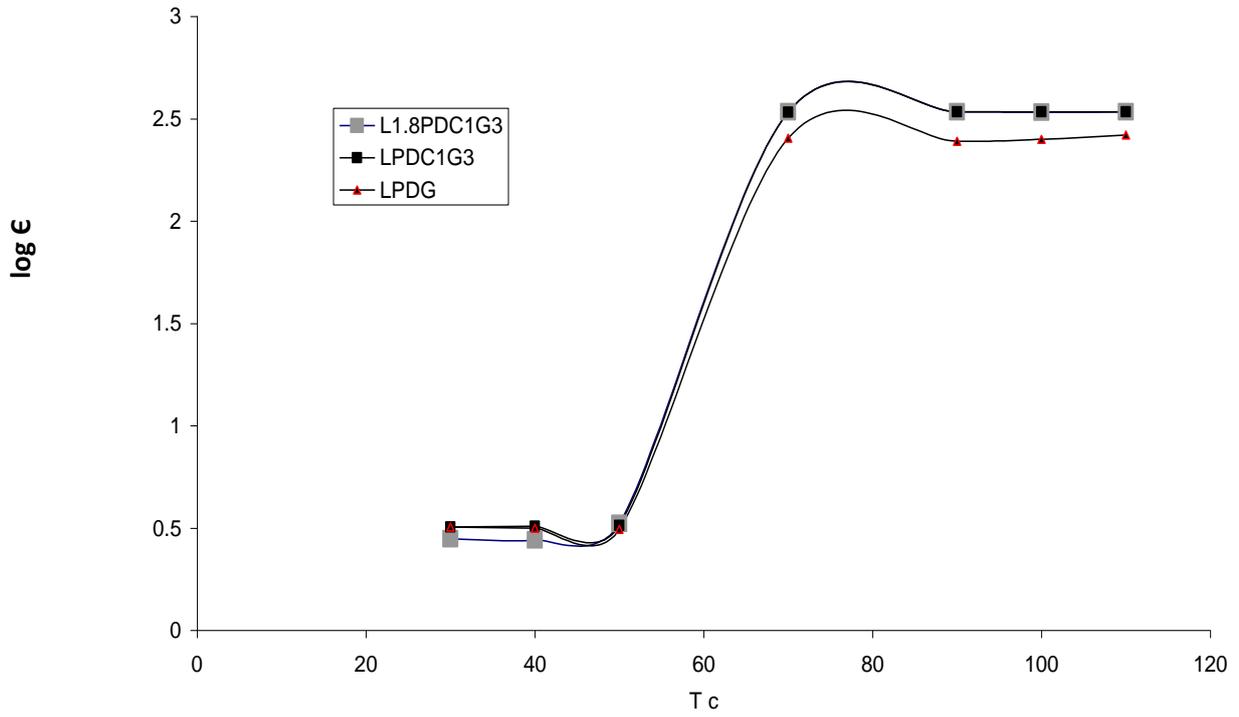


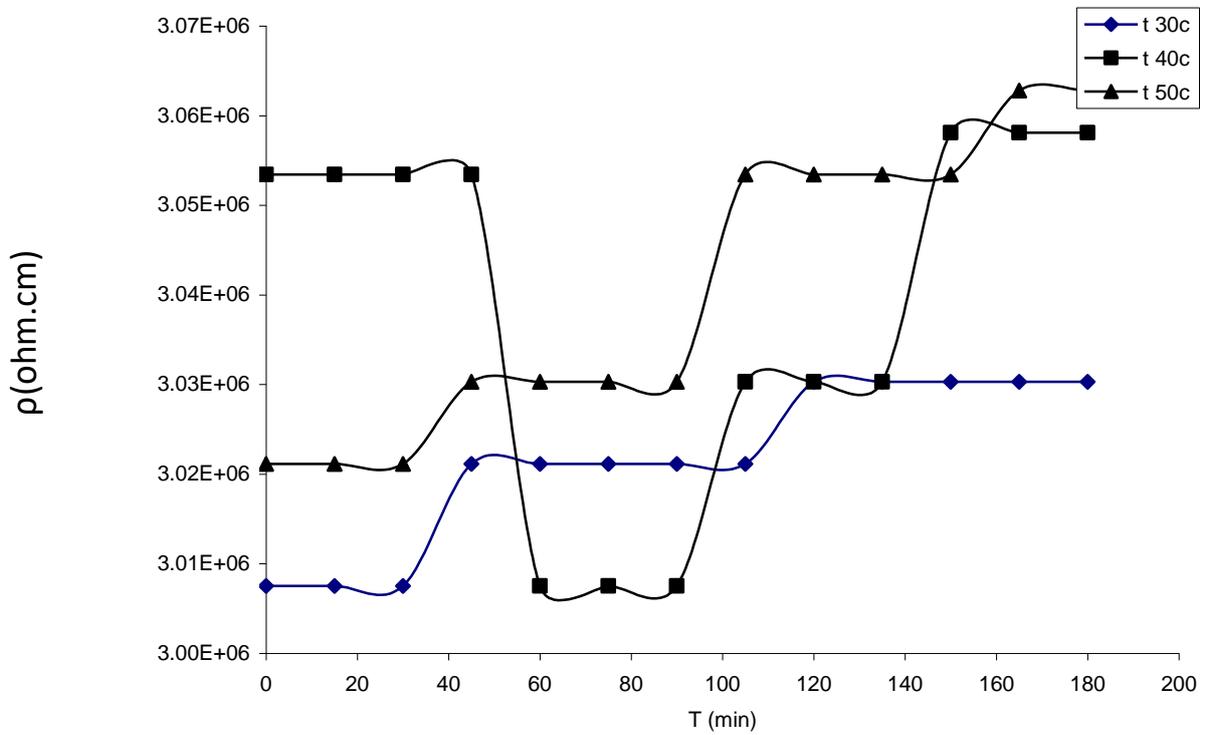
Fig.(۳-۳۰): Relation ship between the permittivity with the time in different temperature of (LPDG)polymer



Fig(۳-۳۱): Relation ship between the resistivity with the temperature for (L_{1.8}PDC₁G₃, LPDC₁G₃,LPDG)polymers



Fig(۳-۳۲): Relationship between the permittivity with the temperature for (L1.8PDC1G3, LPDC1G3, LPDG) polymers



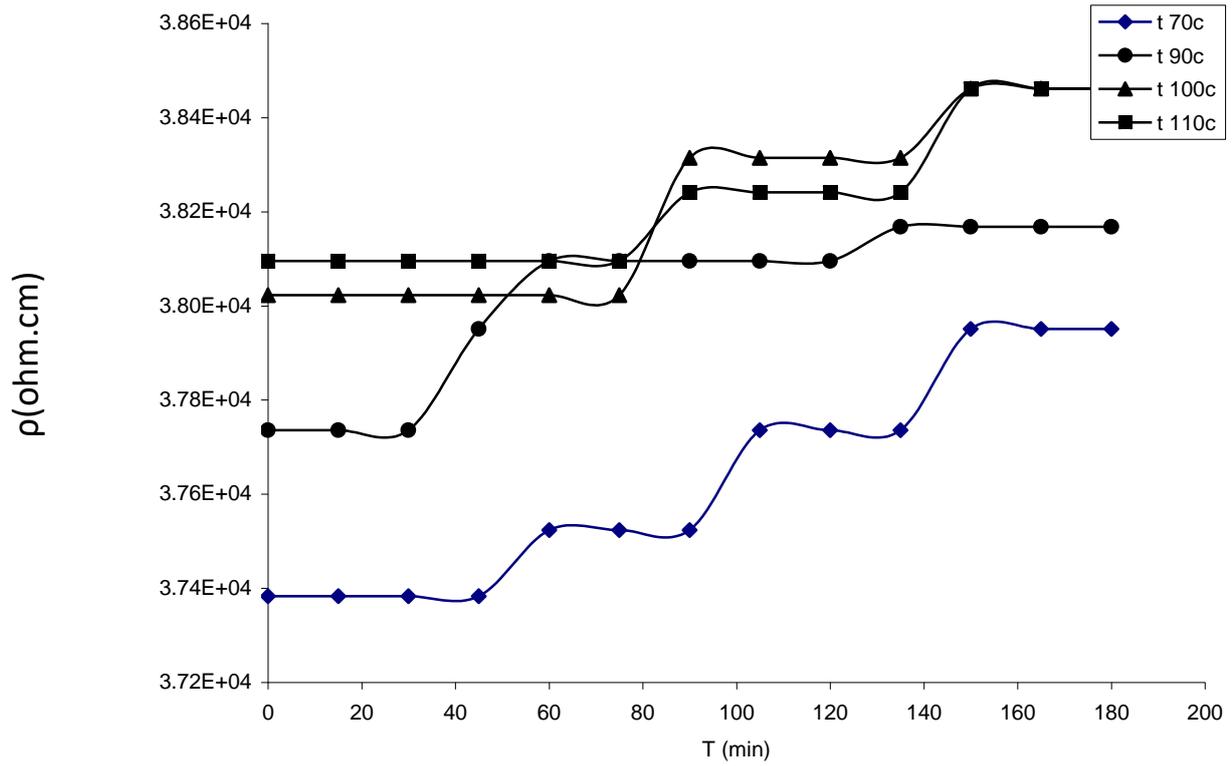
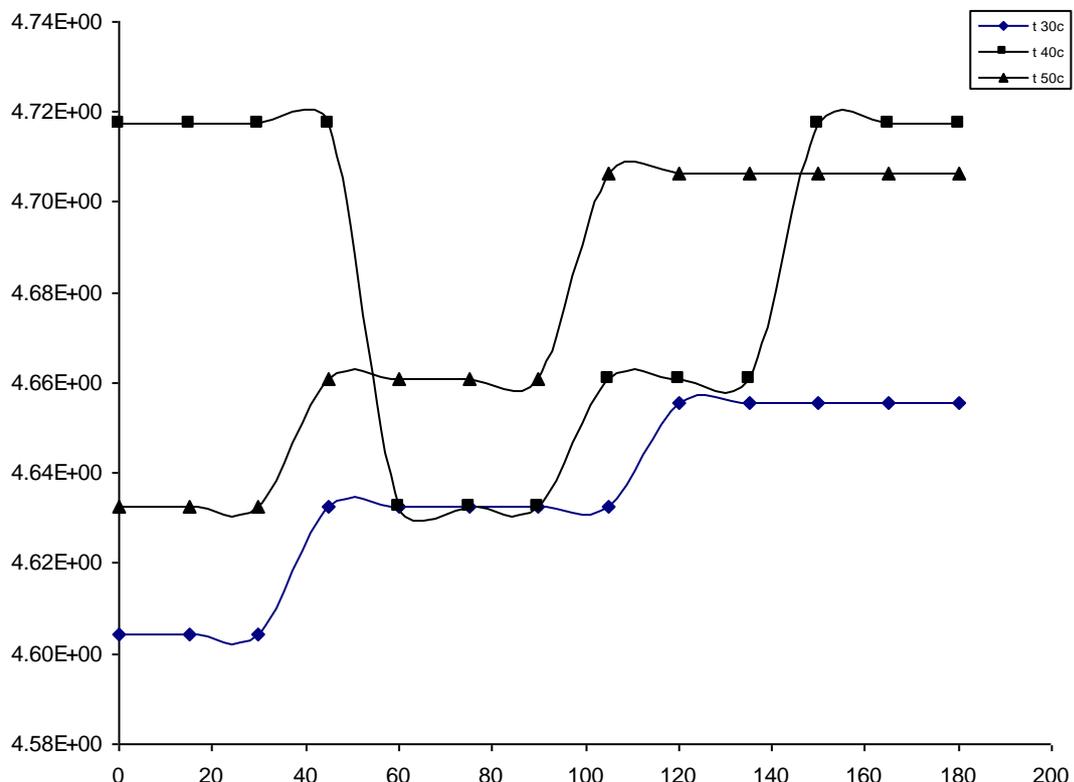


Fig.(۳-۳۳): Relation ship between the resistivity with the time in different temperature of (H_{1,Δ}PDCG)polymer



ε

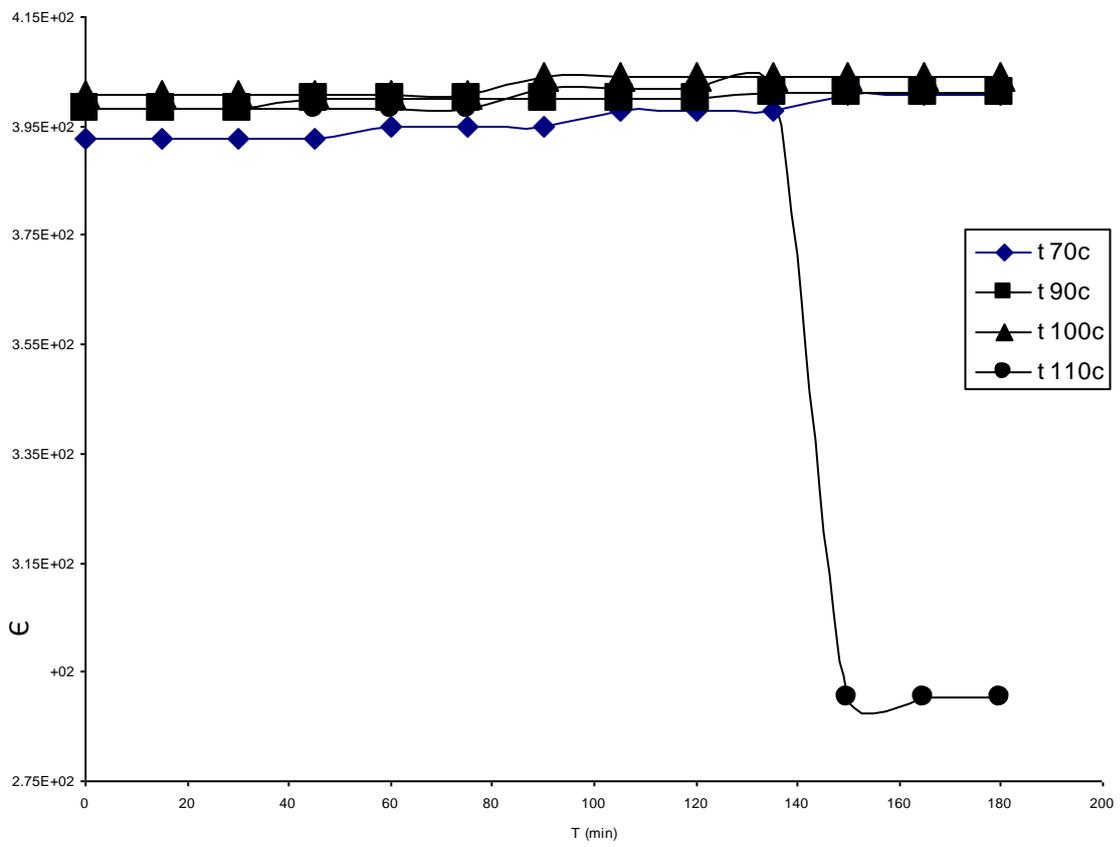
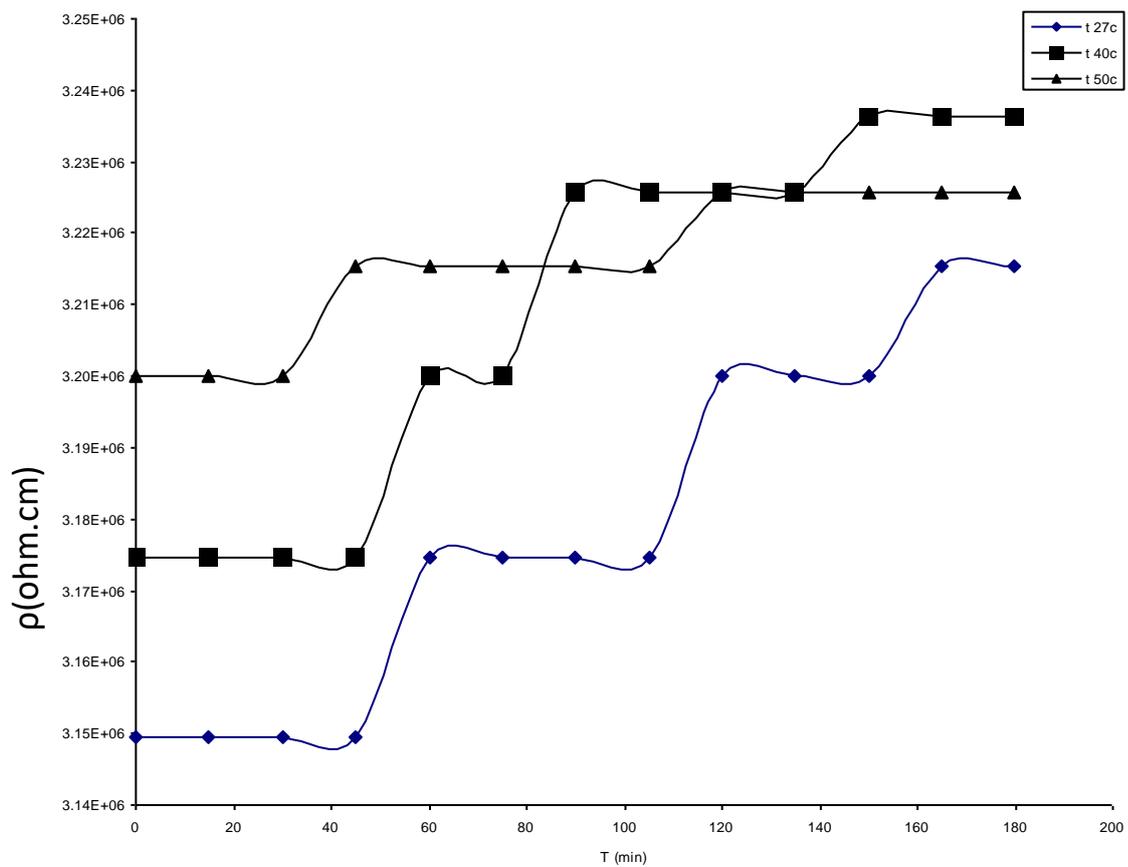


Fig.(۳-۳۴): Relation ship between the permittivity with the time in different temperature of (H_{1,Δ}PDCG)polymer



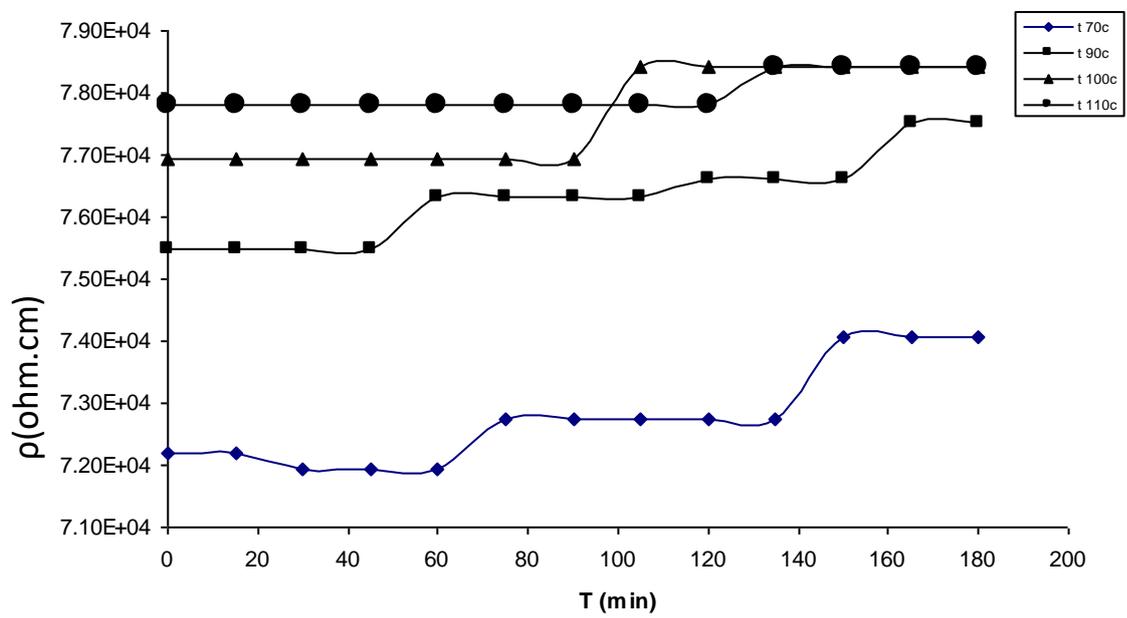
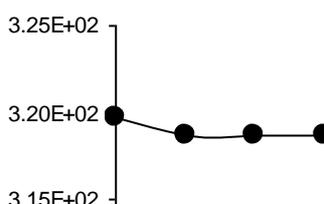
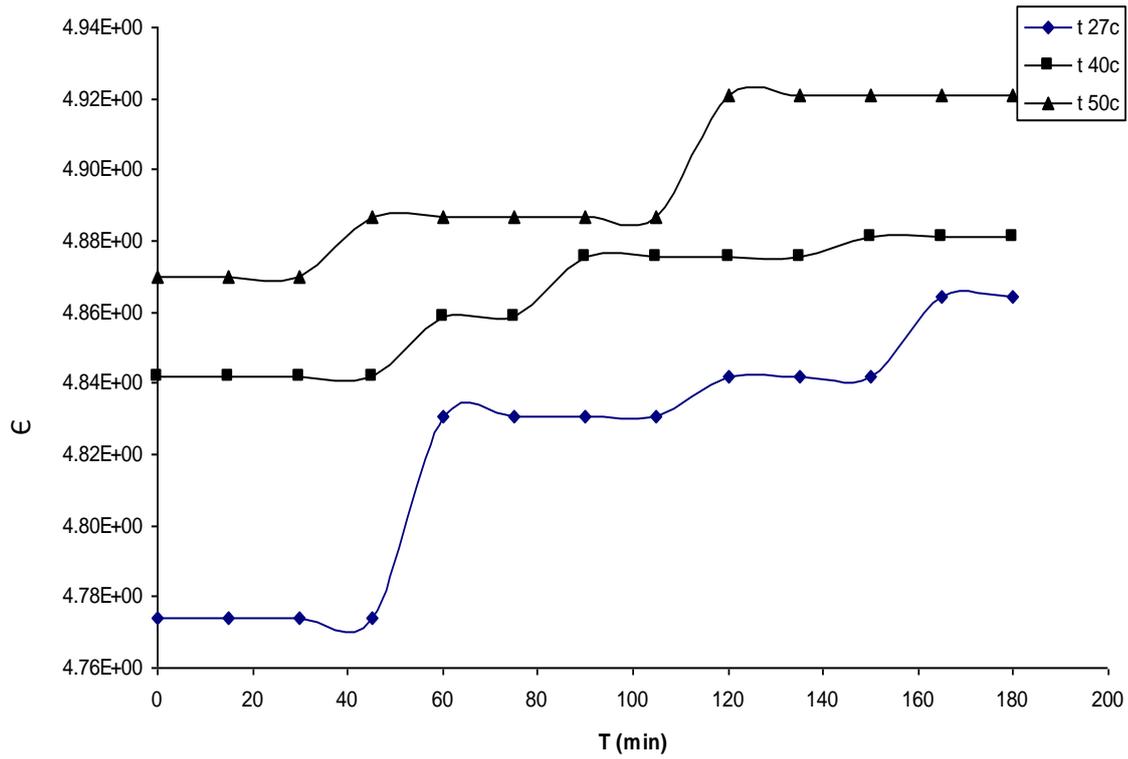
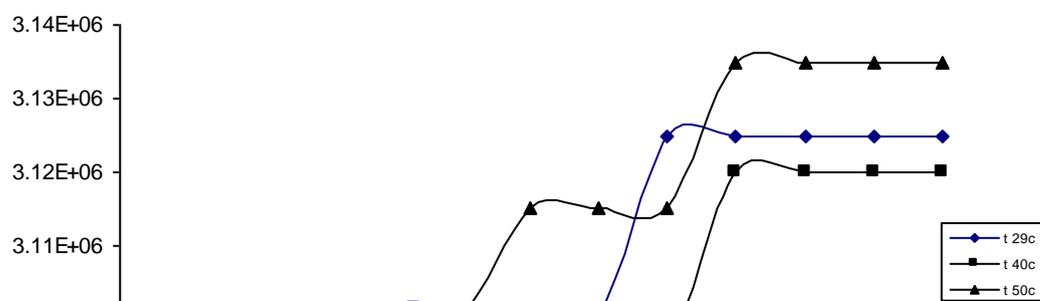


Fig.(۳-۳۰): Relationship between the resistivity with the time in different temperature of (H_{۱۱},PDCG)polymer



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Fig.(۳-۳۶): Relation ship between the permittivity with the time in different temperature of (H_{۱,۴}PDCG)polymer



$\rho(\text{ohm.cm})$

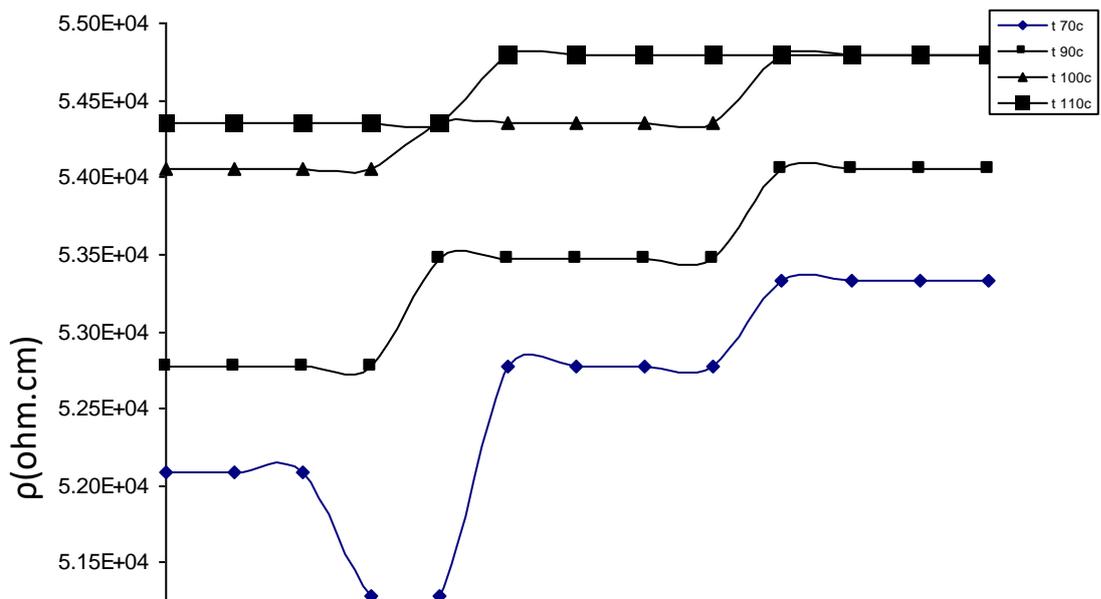
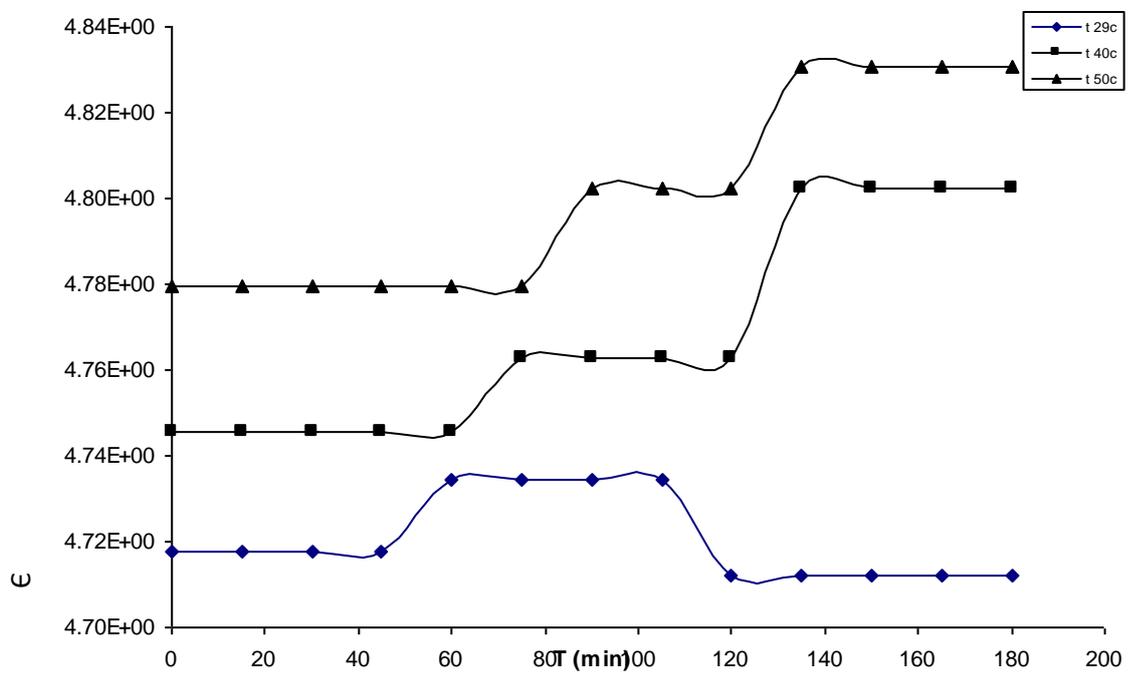


Fig.(۳-۳۷): Relationship between the resistivity with the time in different temperature of (HPDCG)polymer



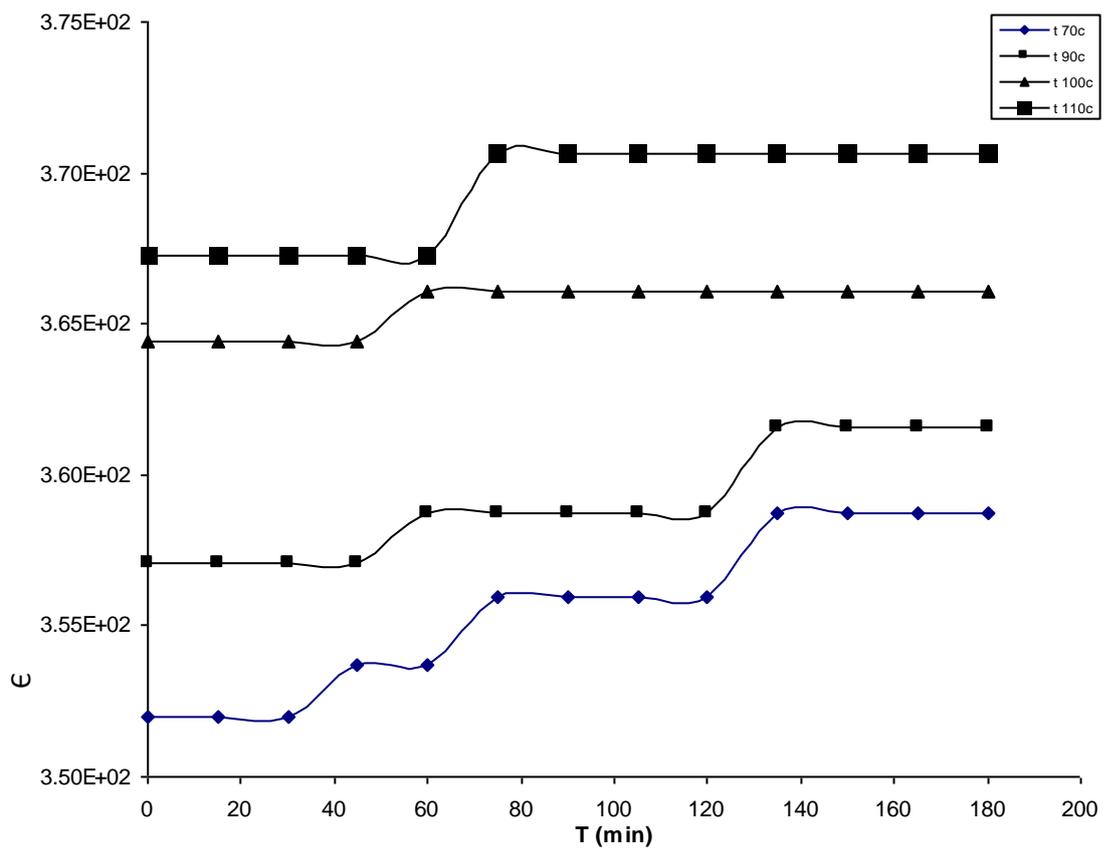
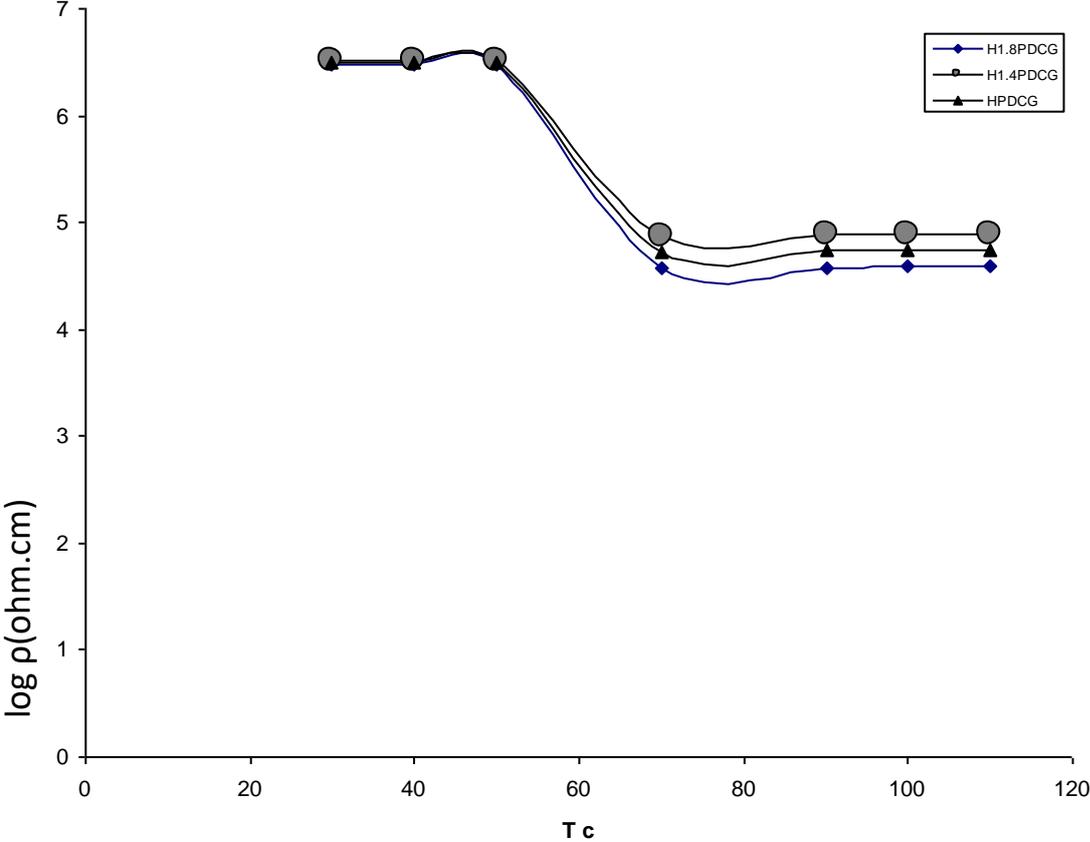
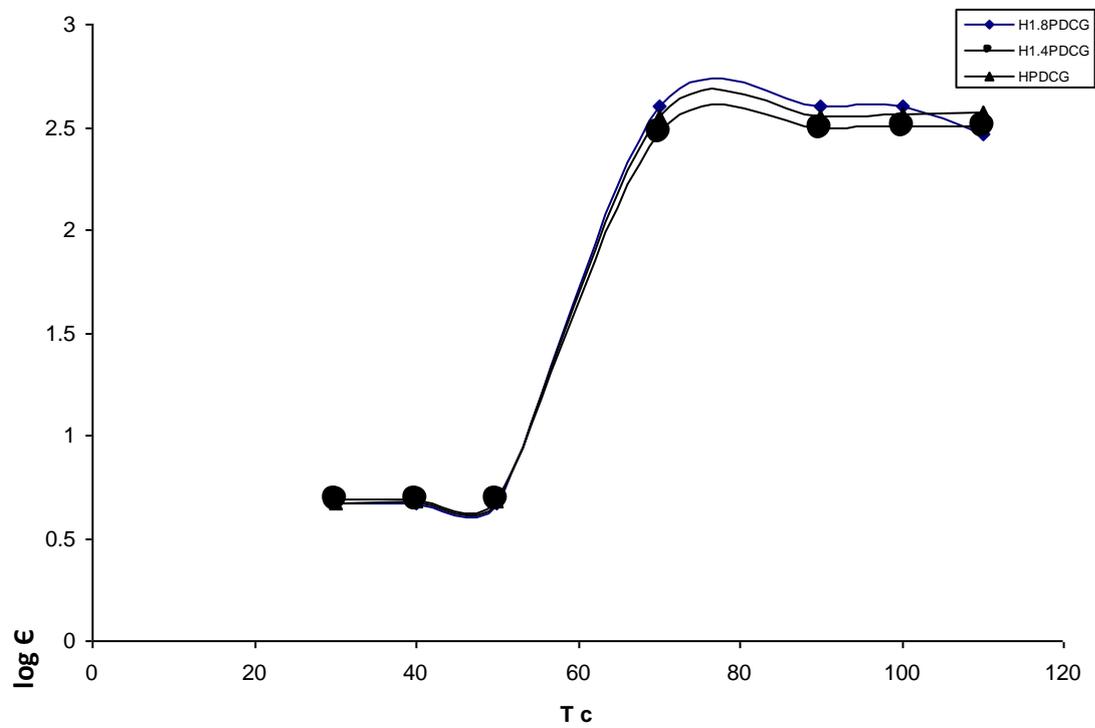


Fig.(3-3^): Relation ship between the permittivity with the time in different temperature of (HPDCG)polymer



Fig(3-39): Relationship between the resistivity with the temperature for (H_{1.8}PDCG, H_{1.4}PDCG,HPDCG)polymers



Fig(3-4): Relationship between the permittivity with the temperature for (H_{1,2}PDCG, H_{1,3}PDCG,HPDCG)polymers

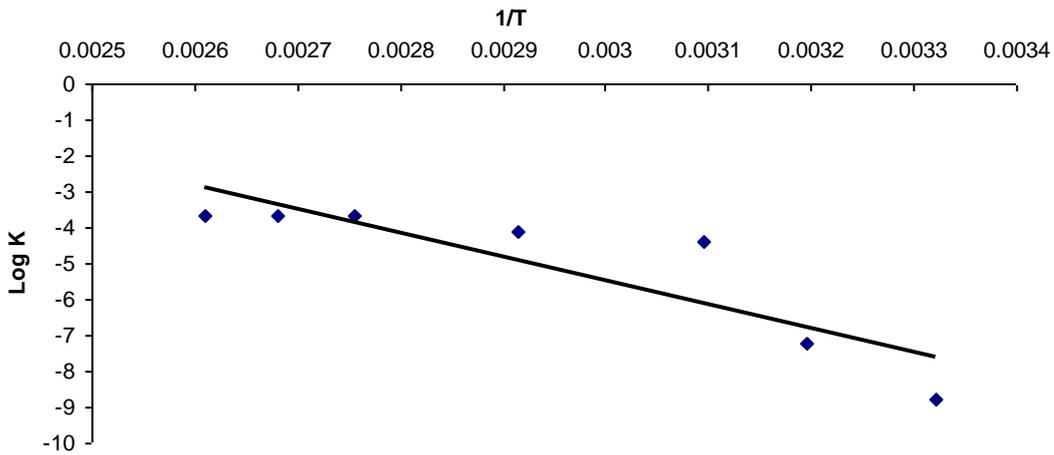


Fig.(3-5): Relationship between the specific conductive (k) with the temperature (K)for [LPDC]

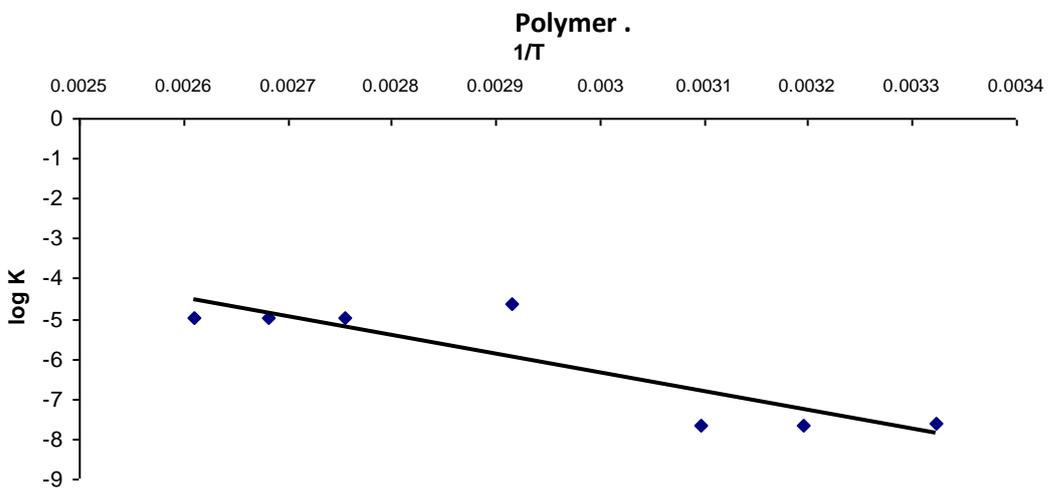


Fig. (3-4): Relation ship between the specific conductive (k) with the temperature (K)for [L₁, PDC]

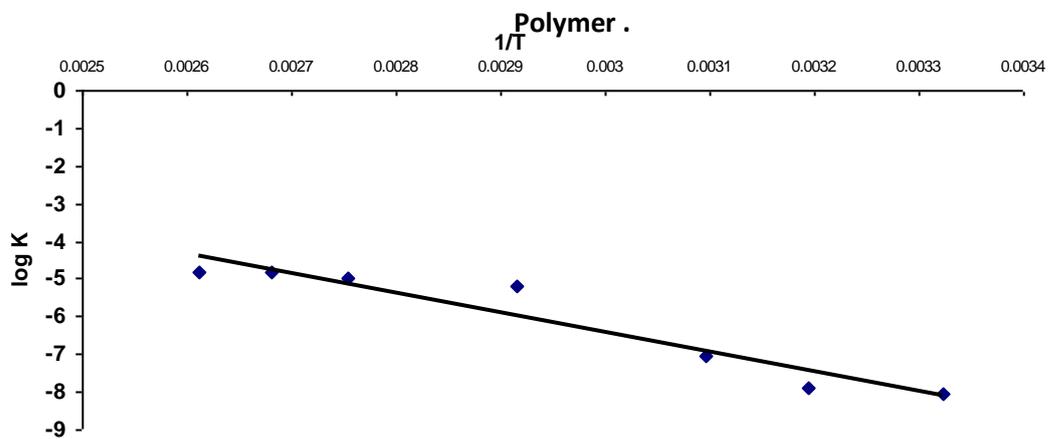


Fig. (3-5): Relation ship between the specific conductive (k) with the temperature (K)for [L₁, PDC]

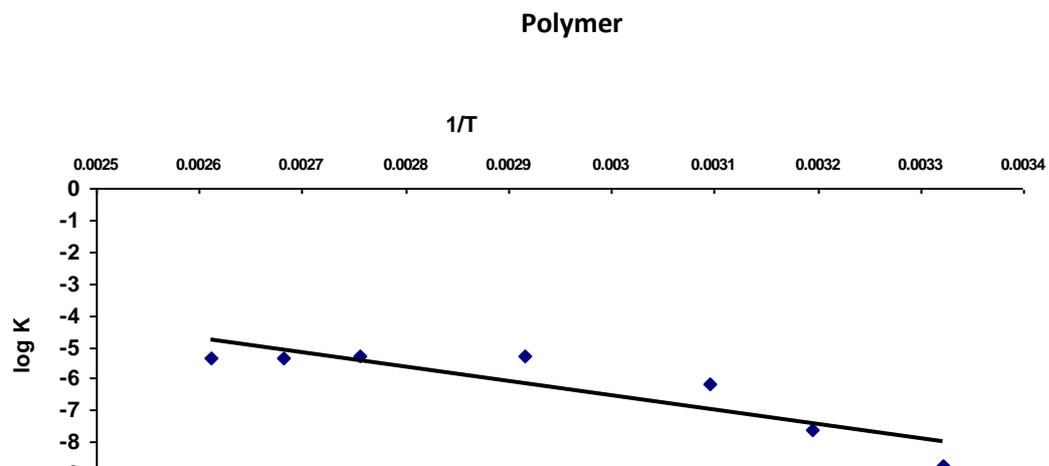


Fig.(٣-٤٤): Relationship between the specific conductive (k) with the temperature (K)for [L₁,PDC-G₁] Polymer .

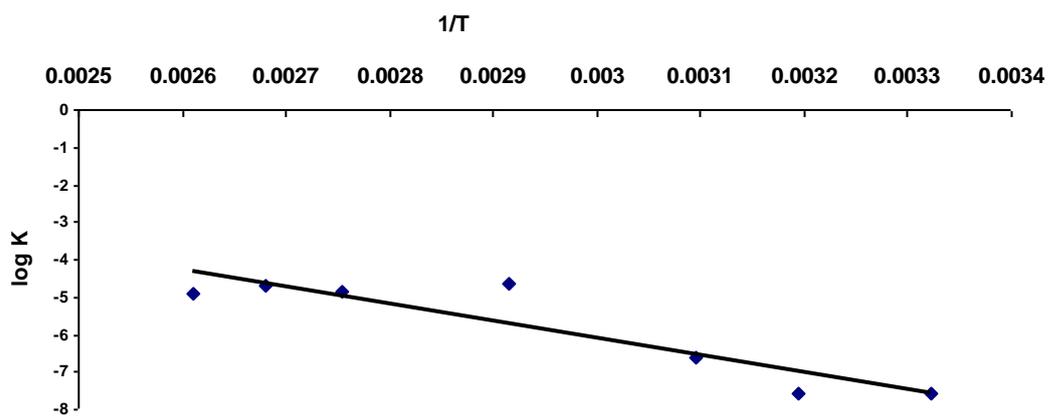


Fig.(۳-۴۵): Relation ship between the specific conductive (k) with the temperature (K)for [L_{۱۰}:PDCrG_۱] Polymer .

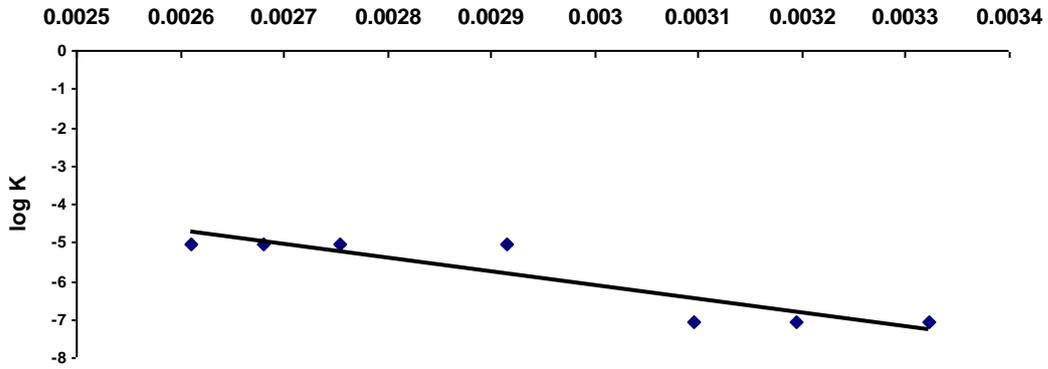


Fig.(۳-۴۶): Relation ship between the specific conductive (k) with the temperature (K)for [LPDCrG_۱] Polymer .

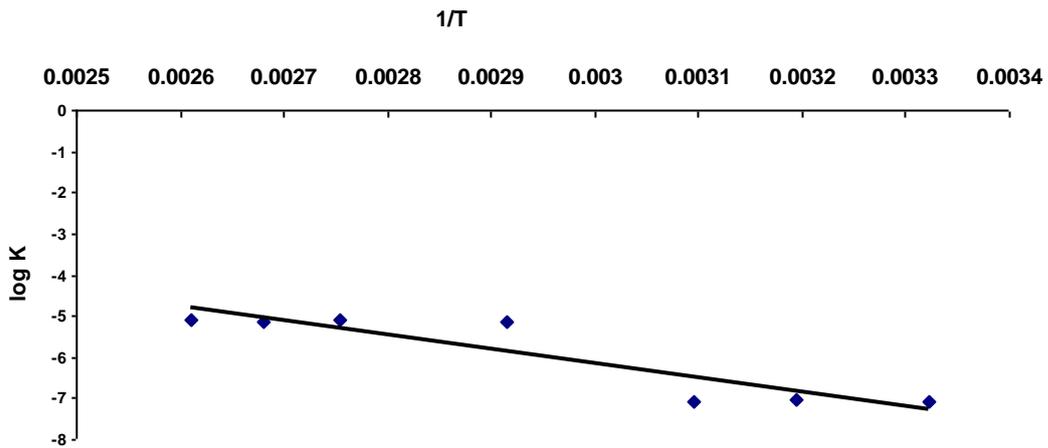


Fig.(3-4): Relation ship between the specific conductive (k) with the temperature (K)for [L_{1,4}PDCG] Polymer .

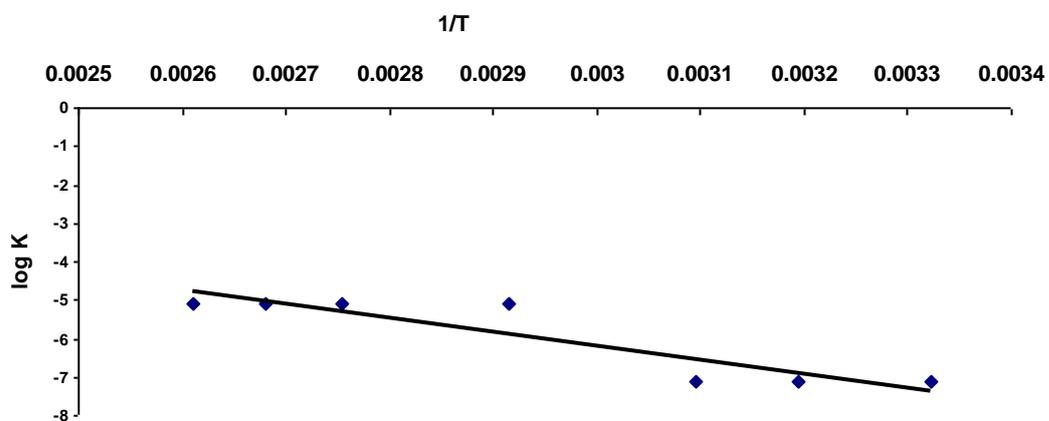


Fig.(3-5): Relation ship between the specific conductive (k) with the temperature (K)for [L_{1,4}PDCG] Polymer .

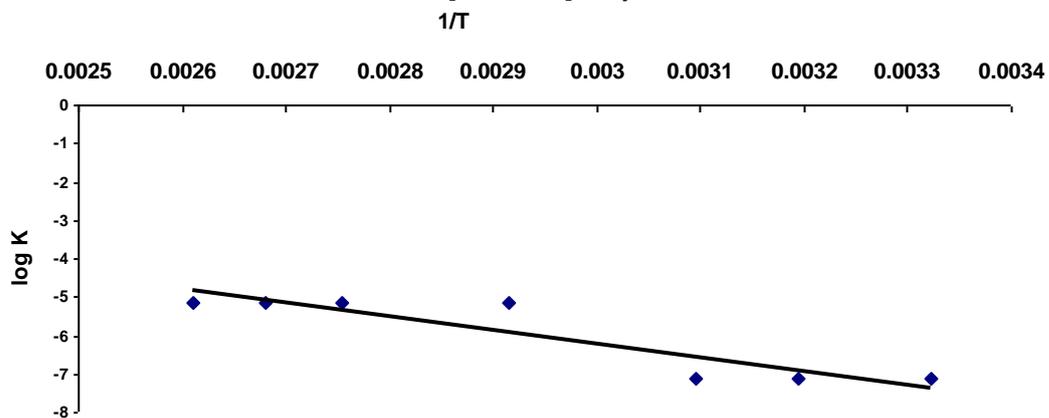


Fig.(3-4): Relation ship between the specific conductive (k) with the temperature (K)for [LPDCG] Polymer .

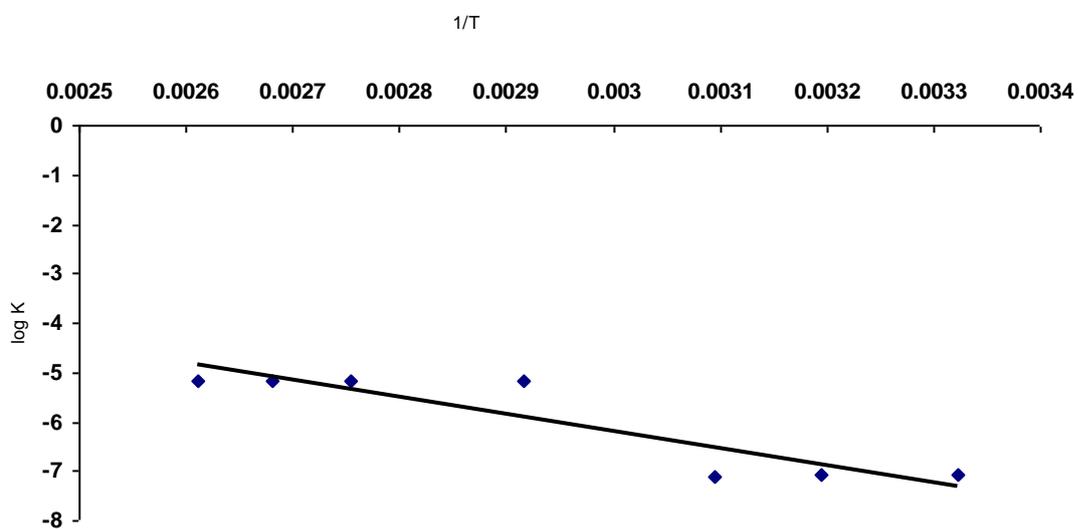


Fig.(3-5): Relation ship between the specific conductive (k) with the temperature (K) for [L_{1,2}PDC.G₊] Polymer .

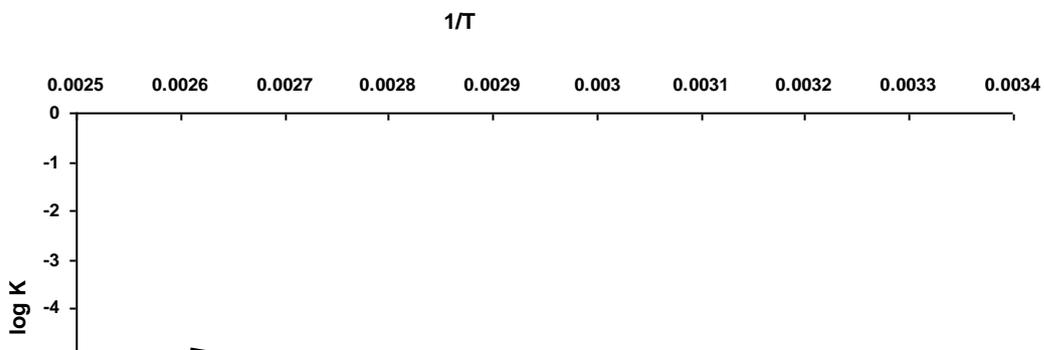


Fig.(٣-٥١): Relation ship between the specific conductive (k) with the temperature (K)for [LPDC,G-] Polymer .

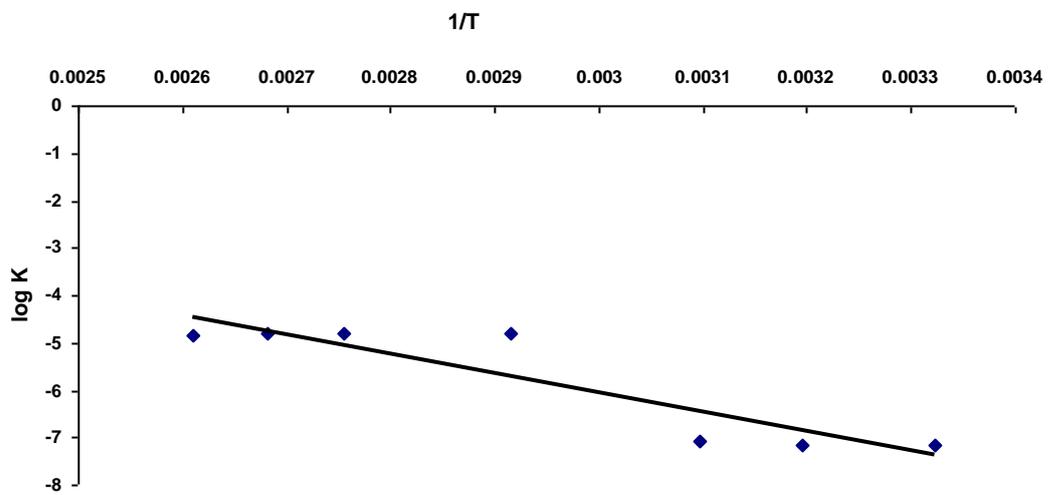


Fig.(۳-۵۲): Relation ship between the specific conductive (k) with the temperature (K)for [LPDG] Polymer

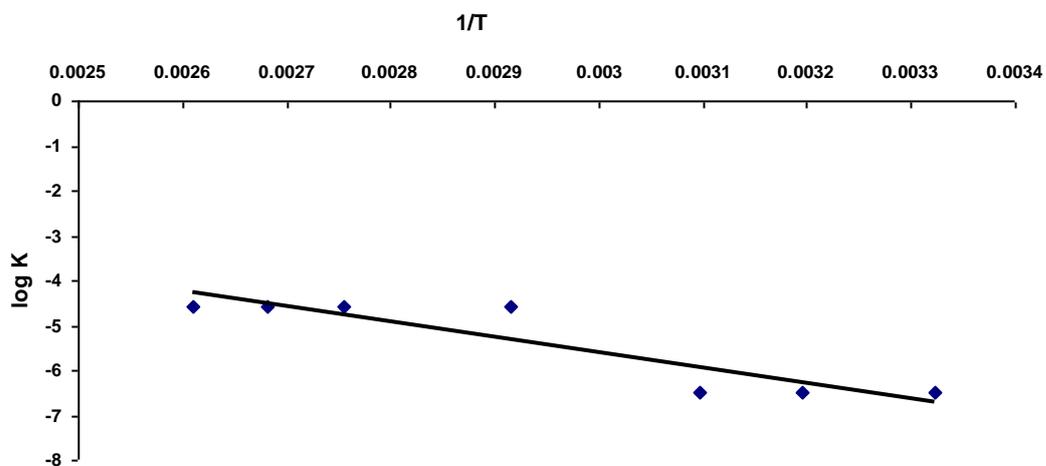


Fig.(۳-۵۳): Relation ship between the specific conductive (k) with the temperature (K)for [HVA/PDCG] Polymer .

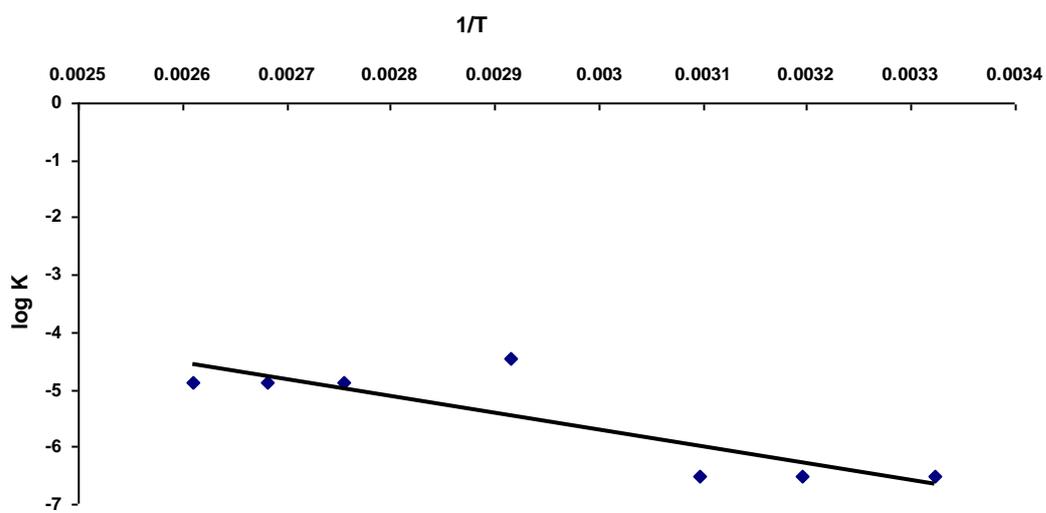


Fig.(3-9): Relation ship between the specific conductive (k) with the temperature (K)for [H₁₂PDCG] Polymer .

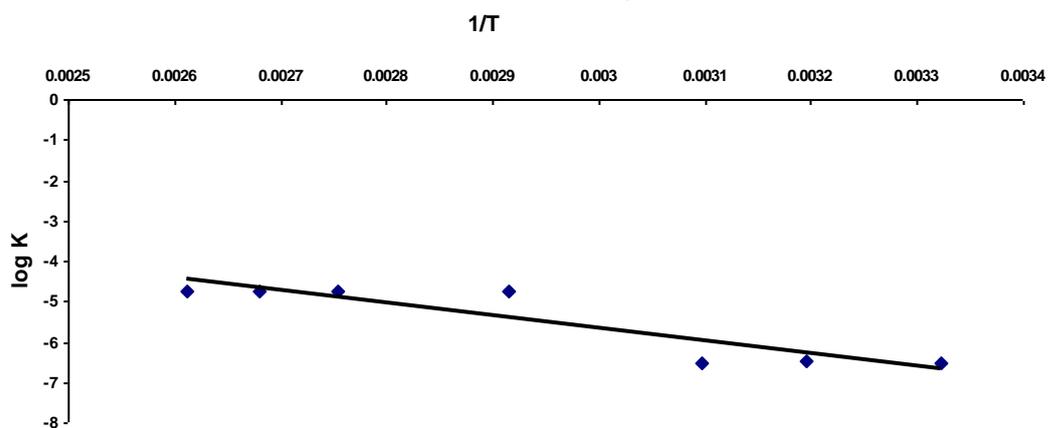


Fig.(3-10): Relation ship between the specific conductive (k) with the temperature (K) for [HPDCG] Polymer

Table (3-1): Represent the practical activation energy for prepared polymers .

No.	Polymer Name	Activation Energy ΔU(Kcal /mol)
۱-	LPDC	۱۲۲.۴۸۲
۲-	L _{۱,۴} PDC	۹۱.۸۶۲
۳-	L _{۱,۸} PDC	۱۰۲.۰۶۲
۴-	L _{۱,۸} PDC _r G _۱	۸۴.۲۰۶
۵-	L _{۱,۴} PDC _r G _۱	۸۶.۱۲۰
۶-	LPDC _r G _۱	۶۸.۸۹۶
۷-	L _{۱,۸} PDCG	۶۶.۹۸۲
۸-	L _{۱,۴} PDCG	۶۸.۸۹۶
۹-	LPDCG	۶۶.۹۸۲
۱۰-	L _{۱,۸} PDC _۱ G _r	۶۶.۹۸۲
۱۱-	LPDC _۱ G _r	۶۶.۹۸۲
۱۲-	LPDG	۷۶.۰۰۱
۱۳-	H _{۱,۸} PDCG	۶۴.۳۱۰
۱۴-	H _{۱,۴} PDCG	۵۷.۴۱۳
۱۵-	HPDCG	۶۳.۷۹۳

Table (3-2): Represent the Conductivity for prepared polymers .

No.	Polymer Name	σ (S / cm)
1-	LDPE	1.000×10^{-16}
2-	LPDC	0.210×10^{-3}
3-	L _{1,ε} PDC	0.103×10^{-4}
4-	L _{1,λ} PDC	0.101×10^{-4}
5-	L _{1,λ} PDC _r G ₁	0.000×10^{-0}
6-	L _{1,ε} PDC _r G ₁	0.132×10^{-4}
7-	LPDC _r G ₁	0.900×10^{-0}
8-	L _{1,λ} PDCG	0.770×10^{-0}
9-	L _{1,ε} PDCG	0.701×10^{-0}
10-	LPDCG	0.770×10^{-0}
11-	L _{1,λ} PDC ₁ G _r	0.724×10^{-0}
12-	LPDC ₁ G _r	0.689×10^{-0}
13-	LPDG	0.149×10^{-4}
14-	H _{1,λ} PDCG	0.262×10^{-4}
15-	H _{1,ε} PDCG	0.128×10^{-4}
16-	HPDCG	0.184×10^{-4}

3-2 Mechanical properties

3-2-1 Effect of fillers on the mechanical properties of LDPE

and HDPE

Two type of filler used to study the effect of carbon black (C) and graphite (G) on the mechanical properties . From figures following , show that increasing of the percentages of carbon black and graphite leads to increase the tensile strength up to (40%) above this percentage no change in tensile strength , also from the same figures show that the value of tensile strength when using graphite (G) are more than when using carbon black (C) as filler , may be due to lubricating character of the graphite (G) also the same results obtained when using mixing of both filler directly with LDPE (i.e increasing the value of tensile strength when increase the percentage of mixing fillers) .

3-2-2 Effect of fillers on the tensile strength of LDPE and HDPE

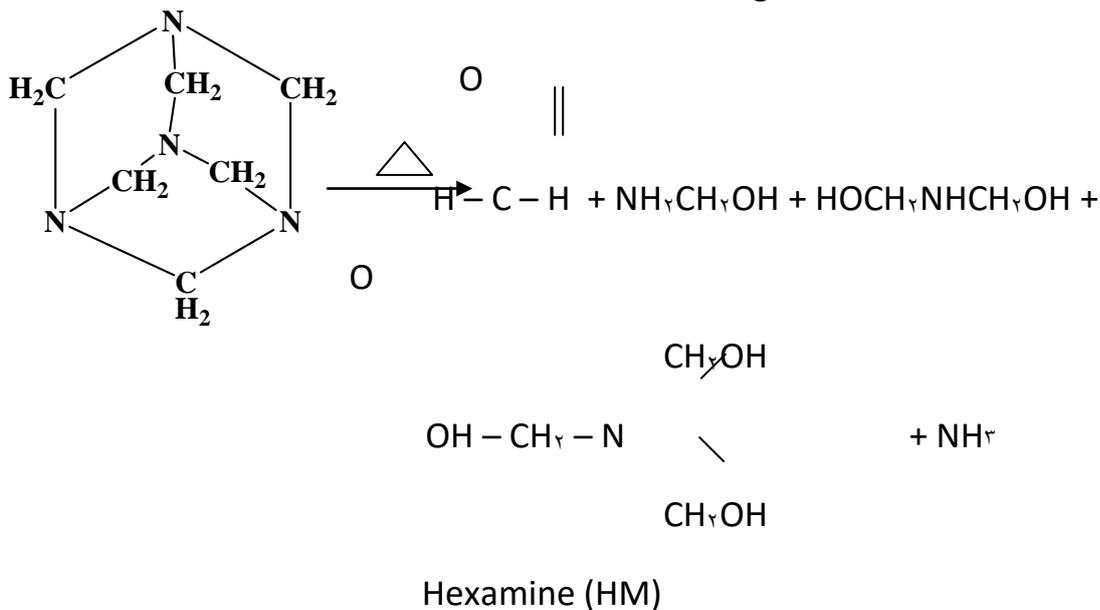
Fig.(3-56) show the effect of (wt.%) filler (C & G) on the tensile strength of LDPE , the result show the tensile strength increase nearly by increasing (wt.%) of these filler because the presence of the filler on the LDPE decrease the free volume and then leads to increase tensile strength but the value of tensile strength when used (G) are some weight more than when used (C)⁽³⁻⁵⁶⁾ .

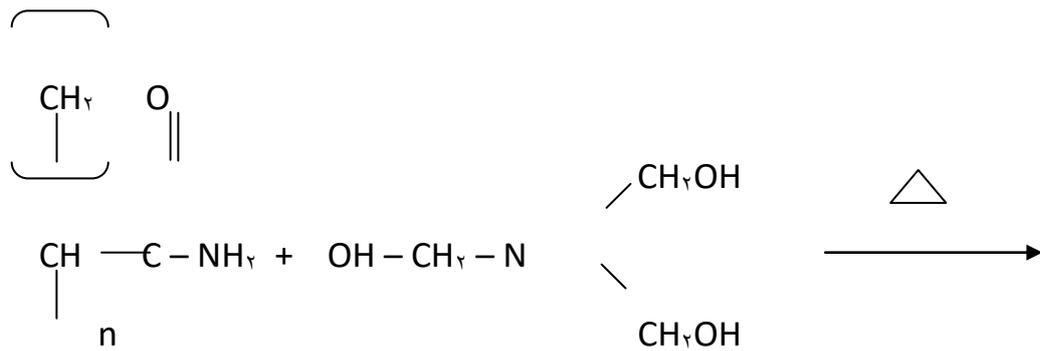
The same result obtained when used (C & G) as hybrid fillers for LDPE , i.e also the tensile strength increase smaller with increasing(wt.%) of hybrid fillers . Fig.(3-57) show the behaviors of this effect .

Fig.(3-18) show the effect of (wt.%) filler (C & G) on the tensile strength of HDPE , the result show the tensile strength increase nearly by increasing (wt.%) of these filler because the presence of the filler on the HDPE decrease the free volume and then leads to increase tensile strength but the value of tensile strength when used (G) are some weight more than when used (C)⁽³⁰⁾ .

Fig.(3-19) show the effect of (LDPE + PAM) with different percentage of hexamine (HM) , from the result showing that :

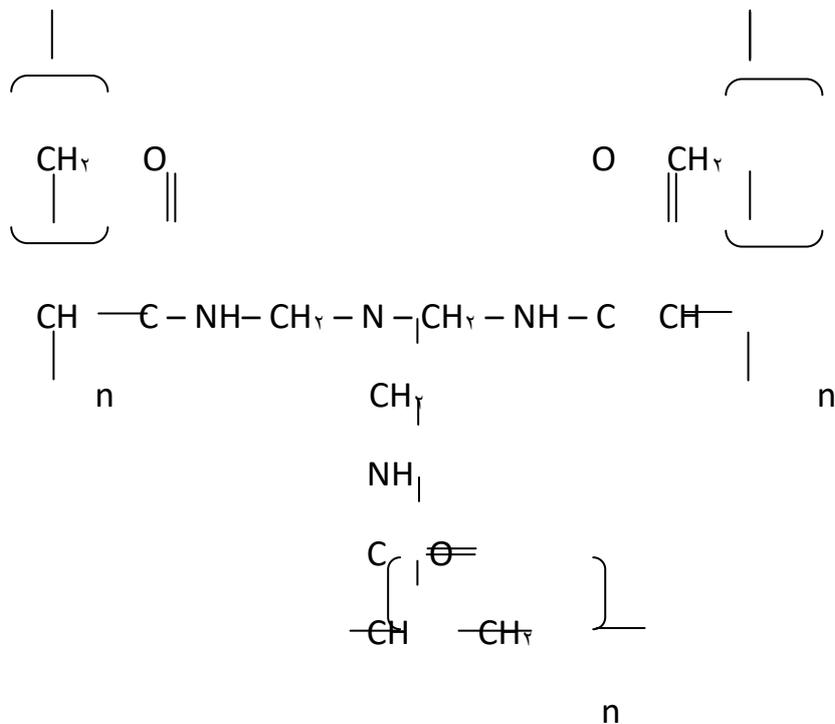
- The tensile strength decrease with increase all percentage of hexamine (HM) this due to more cross linking also .
- The tensile strength for LDPE when used (1 & 3 wt.%) PAM are smaller than when used (3 wt.%) PAM , but still the value for all are less than for LDPE alone⁽³⁰⁾ . The cross linking reaction are :



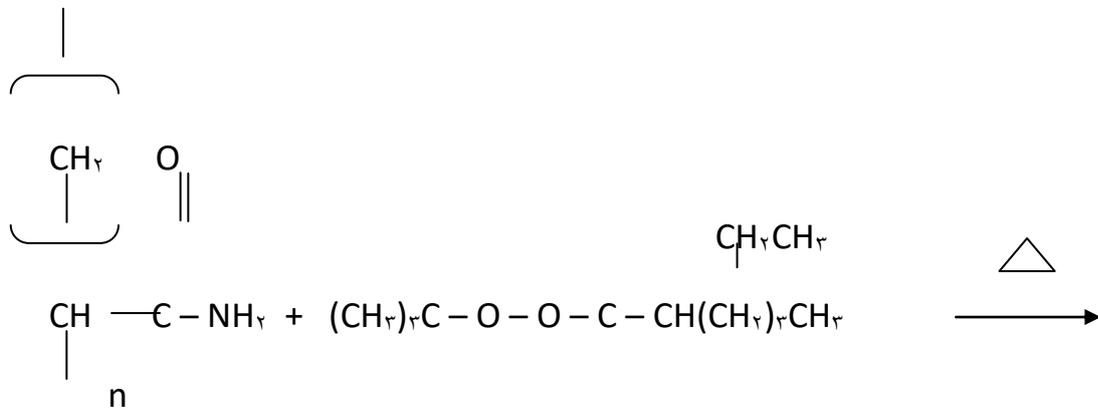


Polyacrylamide(PAM)

Hexamine (HM)

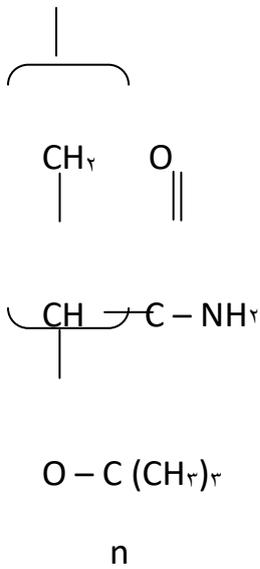


In one the study , the effect of (wt.%) PAM on the tensile strength for the (LDPE with different wt.% C_{r,v}) . Fig.(³⁻¹⁰) show in general no change in tensile strength for the LDPE with different percentage of (C_{r,v}) except for (4.0 wt.% C_{r,v}) when the percentage of PAM is (1%) this means that this percent was the more toughness than other percentage (³⁰⁶) . The cross linking reaction are :



PAM

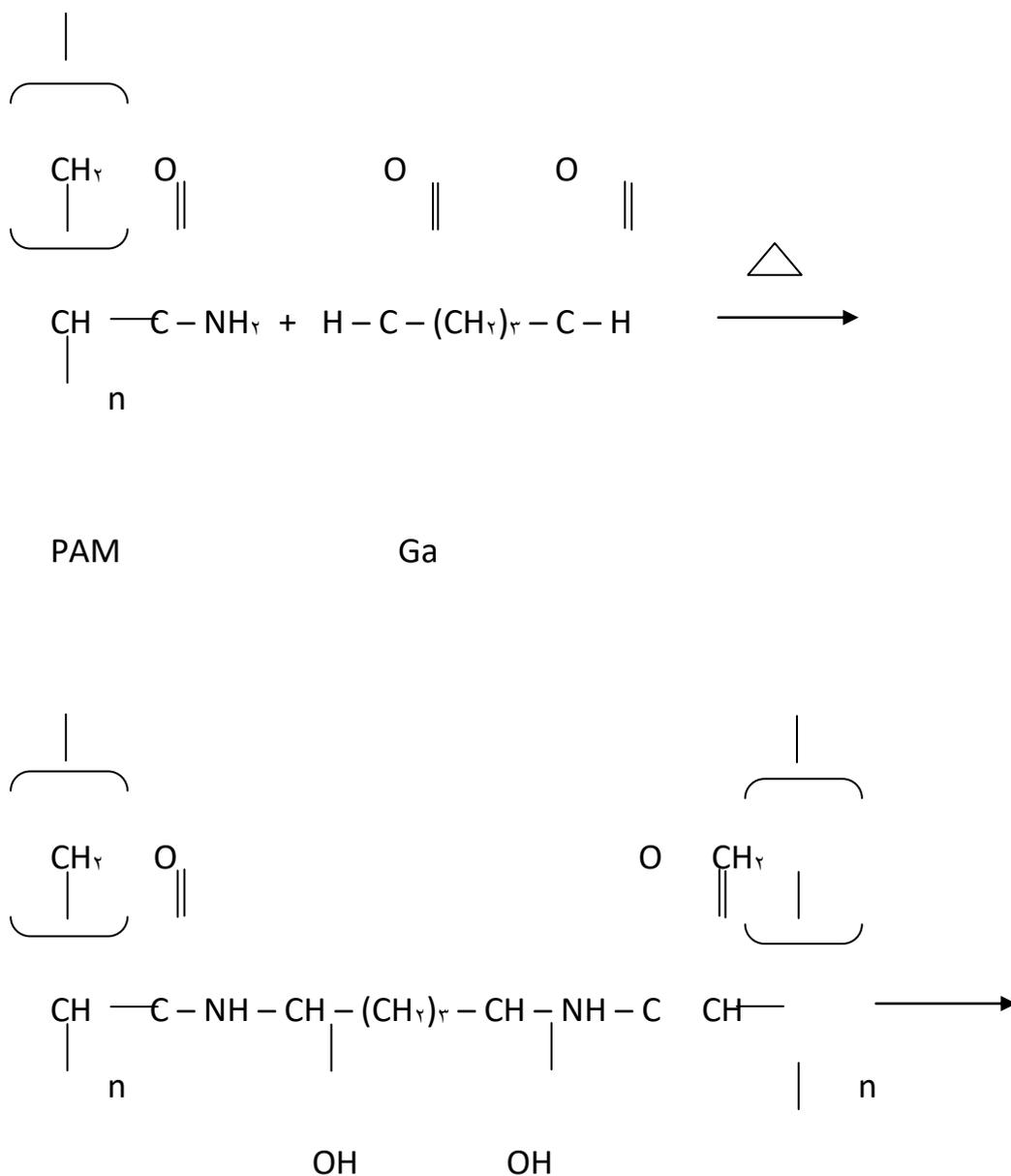
C_r



Also Fig.(3-61) show the effect of different (wt.%) of PAM on the tensile strength for the (LDPE with different wt.% G. aldehyde) . The result

show that the maximum value of tensile strength for LDPE when the (wt.%) of G. aldehyde is (0%) and for PAM is (2%) i.e (1% PMA) compared with (10% PMA) for LDPE alone , this also due to more toughness at this percent (2%) .

The cross linking reaction are :



3-2-3 Effect of fillers on the impact strength of LDPE and HDPE

Fig.(3-60) show the effect of (wt.%) filler (C & G) on the impact strength of LDPE , from the result show that the value of impact strength decrease with increasing the percentage of fillers , this due to the more brittleness of LDPE with these fillers and the value of impact strength of LDPE filled with graphite (G) slightly more than that for LDPE filled with carbon black (C) because of the lubricating effect of graphite (G)⁽¹¹⁾ .

In general most powdered filler reduced the impact strength because the force concerted in one place leads to crack the sample . The same effect obtained for the impact strength for LDPE filled with different ratio of hybrid fillers (i.e carbon black (C) and graphite (G)). Fig.(3-66) show this effect⁽¹²⁾ .

Fig.(3-67) show the effect of the ratio of hybrid fillers (C & G) on the impact strength of HDPE , and from the result show the impact strength decrease from (40 KJ/m²) for HDPE alone to (10 KJ/m²) when the ratio of there fillers (C & G) is (12.0 % wt.) the same case as above for this trends⁽¹³⁾ .

For LDPE copolymerized with different ratio of (1, 2 and 3% wt. PAM), the impact strength decrease with increasing the wt.% of hexamine (HM) as cross linking agent , because the final polymer structure will be more cross linked with increasing both (PAM & HM) , Fig.(3-68) showed these effects⁽¹¹²⁾ .

Fig.(3-69) show the effect of PAM on the impact strength of LDPE in the presence concentration of G. aldehyde . The result show that the impact strength decreased with increasing ratio of PAM (i.e 4 KJ/m² for LDPE + G. aldehyde to ≈ 17 KJ/m² when the ratio of PAM is 0% wt.) , this because of the copolymerized of LDPE with PAM in the presence of G. aldehyde and then lead to more cross link polymer⁽¹⁰⁷⁾ .

The same trend for impact strength of (LDPE + C₁₂V) with different percentage of PAM are obtained . Also the decreasing of impact strength is due to more cross link during the addition of different percentage of PAM in the presence of C₁₂V as peroxide which lead to cross linked polymer . The result show in Fig.(3-70) .

Figs.(3-71 , 3-72 , 3-73) show the effect of PAM on the impact strength of (LDPE in the presence of G. aldehyde and C₁₂V together) . These figures show reduce the value of impact strength with increasing percentage of PAM , all due to more cross linking occur with increasing ratio of PAM⁽¹⁰⁶⁾ .

3-2-4 Effect of fillers on the elongation of LDPE and HDPE

The failure of material is normally associated with plastic deformation in the form of necking at the breaking point . The amount of elongation is measured for the plain blended matrix as a function of fillers , types of fillers , also degree of blending .

Fig.(3-74) show the presence of hybrid fillers lead to decrease the elongation both in (carbon black (C) and graphite (G)) because these fillers enter the free volume in LDPE and progressive tendency towards brittleness or reduce elongation , also in some time the excess addition of fillers in the matrix would result in the progressive formation of two phase region or (phase separation region) , the excess of the percentage of thesis fillers from (2.0 – 12.0 % wt.) no change in the value of elongation ⁽⁷⁴⁾ .

Fig.(3-75) show the effect of hybrid fillers on the elongation of LDPE , the result show that the value of elongation generally decrease with increasing the percentage of hybrid fillers up to (4.0 % wt.) above this ratio the value of elongation remain constant , while Fig.(3-76) show the same behaviors for HDPE , but the value here less than for LDPE because the HDPE are more crystalline than LDPE and than leads to less value of elongation ⁽⁷⁵⁾ .

In another study , for the effect of polyacryl amide (PAM) on the elongation of LDPE cross linked with hexamine (HM) , the Fig.(3-77) show the behaviors of elongation curves and showing the value decrease with all percentage of PAM (i.e 1, 2 and 3% wt.) , but the of effect of hexamine (HM)

was larger up to (2.5% wt.) , above this the value of elongation remain constant , the reason for decreasing the elongation is due to more cross linking which lead to decrease the elasticity of the final products ⁽²⁰⁹⁾ .

The same behaviors for elongation curve are obtained for (LDPE + G. aldehyde) in the presence of different percentage of PAM , but here the decrease of elongation up to (2% wt. PAM) , above this the value of elongation nearly constant . Fig.(3-78) show there results ⁽²⁰⁶⁾ .

The same trend for elongation of (LDPE + C_{1v}) with different percentage of PAM are obtained . Also the decreasing of elongation is due to more cross link during the addition of different percentage of PAM in the presence of C_{1v} as peroxide which lead to bind the chain of LDPE with the chain of PAM or itself leading to more cross linked polymer . The result show in Fig.(3-79) ⁽²⁰⁸⁾ .

While Figs.(3-80 , 3-81 , 3-82) show the effect of PAM on the elongation of (LDPE in the presence of G. aldehyde and C_{1v} together). There figures show increase the value of elongation with increasing percentage of PAM , all due to more cross linking occur with increasing ratio of PAM ⁽²⁰⁶⁾ .

3-2-5 Effect of fillers on the hardness (shor A) of LDPE and HDPE

The hardness of any materials is generally considered as a surface property , but the shor – hardness is a special parameter exclusively used for polymeric materials to define their resistance to piercing . This would in fact reflect up on about the mechanical integrity of the bulk and in turn up on internal bonding .

Fig.(3-83) show the effect of the fillers on the value of hardness , the result showing that the hardness of LDPE increase when the percentage of fillers (2.5% wt.) for both carbon black (C) and graphite (G) , but the value of hardness when the carbon black (C) as filler more than when the graphite (G) fillers , this is due to lubricant effect of the graphite (G) more than carbon black (C)⁽³⁶⁾ .

In the other hand , the increasing of the percentage of both fillers from (2.5 – 10% wt.) no change in the value of hardness (nearly remain constant) , but in the final percentage (i.e 12.5% wt.) the value of the hardness deviate from the curve especially in the case of graphite (G) as filler , this actually due to non homogeneity of LDPE with graphite (G) during mixing⁽³⁶⁾ .

In Fig.(3-48) show the effect of hybrid fillers on the value of hardness for LDPE and from the result showing that the value of hardness increase when the percentage of carbon black (C) filler more than graphite (G) fillers also this due to the lubricant effect of graphite (G) (34).

While Fig.(3-49) show the effect of hybrid fillers (carbon black (C) 0.5% and graphite (G) 0.5%) on the value hardness of HDPE , the result show that the value of hardness decrease with increasing the percentage of hybrid fillers up to (1.0% wt.) , the hardness will equal to (56 shor A) (i.e the same value for HDPE alone) , finally the value of the hardness decrease with (12.0% wt.) of these fillers .

As abstract the value of hardness decrease this may be due to non homogeneity of the surface of HDPE after mixing with fillers (35).

Fig.(3-50) show the effect of hexamine (HM) as cross linking agent on the hardness of (LDPE with different percentage of PAM) , and from the result the maximum value of hardness when the percentage of (HM) is (2.0% wt. & 1% wt.) of PAM because the (HM) as cross linking agent bonded between (LDPE & PAM) which leads to increase cross linking density , above this the value of hardness decreased , due to formation of porosity formed on decomposition of (HM) by heating .

In the presence of different percentage of G. aldehyde (0, 4.0 and 10% wt.) as cross linking agent on the LDPE with variation of PAM (261) .

Fig.(3-87) show the result of the hardness value and the trend of this value mainly constant with increasing the (% wt.) of PAM except of hardness for all percent of PAM are higher when the percent of G. aldehyde is (4.0% wt.) in the LDPE this mean that this percent give the best cross link density for the polyethylene with PAM (261) .

In another study , the effect of peroxide percentage on the value of hardness for LDPE in the presence of different percentage of PAM .

Fig.(3-88) show these value and the trend the hardness value decrease except for (4.0% wt. C_{1v} and in the presence of 4% wt. PAM) , the maximum hardness value of LDPE , this lead to more cross linking density of the final products , with increasing PAM concentration(for all percentage of C_{1v}) (261) .

While Figs.(3-89 , 3-90 , 3-91) show the effect of PAM on the hardness (shor A) of (LDPE in the presence of G. aldehyde and C_{1v} together) . There figures show increase the value of hardness (shor A) with increasing percentage of PAM , alls due to more cross linking occur with increasing ratio of PAM (261) .

3-2-6 Effect of fillers on the hardness (shor D) of LDPE

and HDPE

Fig.(3-92) show the effect of the two type of filler (carbon black (C) and graphite (G)) on the hardness (shor D) of LDPE from this figure show that the value of the hardness fluctuated during the percentage of these filler (2.0 – 12.0% wt.) this due to non homogeneity of the final surface structures⁽²⁶²⁾.

While Fig.(3-93) show the effect of hybrid fillers on the hardness , and showing that the hardness decrease firstly from (40 shor D) for LDPE alone to (42 shor D) when the percentage of the fillers is 2.0%wt. (20% C + 70% G) , then increased smartly up to (47 shor D) when the percentage of these fillers (12.0% wt.) , the increasing of the hardness leads to decrease the free volume of LDPE⁽²⁰⁸⁾.

Fig.(3-94) show that the hardness of HDPE increased with increasing the ratio of mixed fillers (0.0% C + 0.0% G) up to 7.0% wt. , above this the value of hardness became decrease , i.e the optimum value of hardness is (40 shor D) , this leads to more homogeneity and less free volume at this percentage of fillers⁽²⁶²⁾.

While Fig.(3-95) show the effect of (% wt.) hexamine (HM) on the hardness of (LDPE with different ratio of PAM) , from this figure show these

value is fluctuated with the percentage of hexamine (HM) because of the presence of the porosity in the final surface structures of LDPE and this porosity formed during the decomposition of hexamine (HM) during the heating ^(٢٥٨) .

On the other hand Fig.(٣-٩٦) show the effect of percentage of PAM on the hardness of (LDPE + G. aldehyde) . The result showing that the value of hardness decrease with increasing (% wt.) of PAM (١ – ٢% wt.) , while in the (٣% wt. of PAM) give the maximum value of the hardness of (LDPE with all percentage of G. aldehyde) , than the hardness decrease with increasing (% wt. of PAM) . This means that the optimum condition for the hardness of LDPE when the percentage of G. aldehyde is (٧.٥% wt.) while for PAM is (٣% wt.) because this ratio give the best cross linking for LDPE ^(٢٦٢) .

Fig.(٣-٩٧) show the effect of percentage of PAM on the hardness of (LDPE + C_{٦٧}) . The result showing that the value of hardness decrease with increasing (% wt.) of PAM (١ – ٢% wt.) , while in the (٣% wt. of PAM) give the maximum value of the hardness of (LDPE with all percentage of C_{٦٧}) , than the hardness decrease with increasing (% wt. of PAM) . This means that the optimum condition for the hardness of LDPE when the percentage of C_{٦٧} is (٧.٥% wt.) while for PAM is (٣% wt.) because this ratio give the best cross linking for LDPE ^(٢٦٢,٢٦٣) .

While Figs.(3-98, 3-99, 3-100) show the effect of PAM on the hardness (shor D) of (LDPE in the presence of G. aldehyde and C_{1v} together) . These figures show decrease the value of hardness (shor D) with increasing percentage of PAM , all due to more cross linking occur with increasing ratio of PAM (20%).

3-2-7 IR Spectra

Fig.(3-9) show the FTIR spectra for to(LAMHM) polymer , the appearance of a new strong peak in the frequency range (3300 cm⁻¹) for to primary substitute amide , also disappearance moderate two peaks in the frequency range (3400 , 3000)cm⁻¹ for unsubstitute amide and disappearance broad peak in the frequency range (3400 - 3600)cm⁻¹ for (OH⁻) group , this indicate the formation polymer cross linking .

Fig.(3-10) show the FTIR spectra for to(LAMC_{1v}) polymer , the appearance of a new strong peak in the frequency range (1600 cm⁻¹) due to (C = N) bond , also disappearance moderate two peaks in the frequency range (3400 , 3000)cm⁻¹ for unsubstitute amide this indicate the formation polymer cross linking .

Fig.(۲-۱۱) show the FTIR spectra for to(LAMGa) polymer , the appearance of a new moderate peak in the frequency range ($۳۴۵۰\text{ cm}^{-۱}$) for to primary substitute amide, also disappearance moderate two peaks in the frequency range ($۳۴۰۰ , ۳۵۰۰\text{ cm}^{-۱}$) for unsubstitute amide and disappearance broad peak in the frequency range ($۳۴۰۰ - ۳۶۰۰\text{ cm}^{-۱}$) for (OH^-) group , this indicate the formation polymer cross linking .

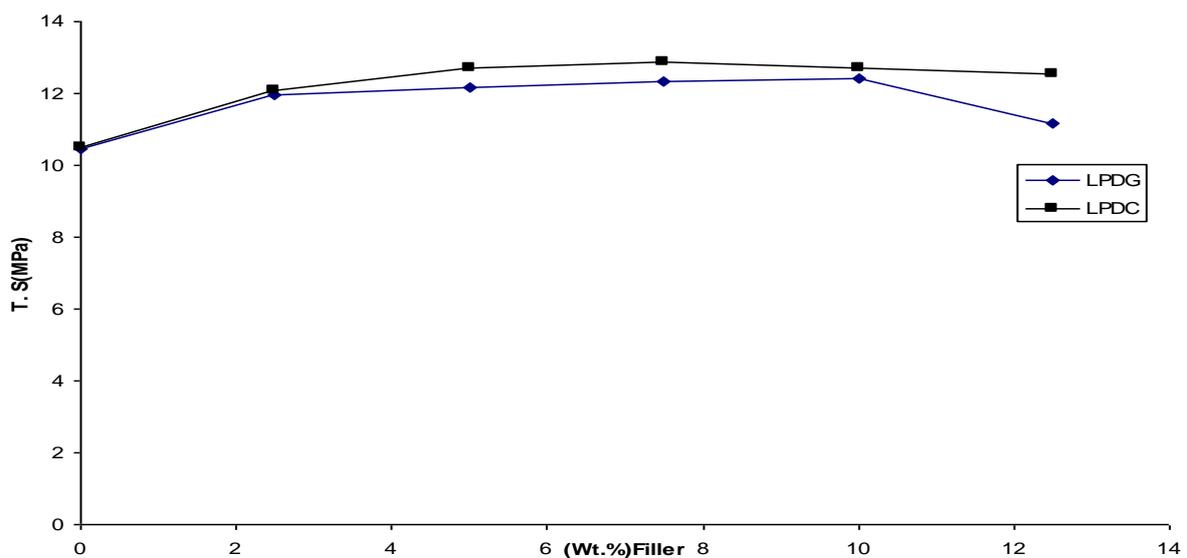


Fig.(۳-۵۶):Effect of fillers on the Tensile Strength of LDPE for [LPDG , LPDC] Polymers .

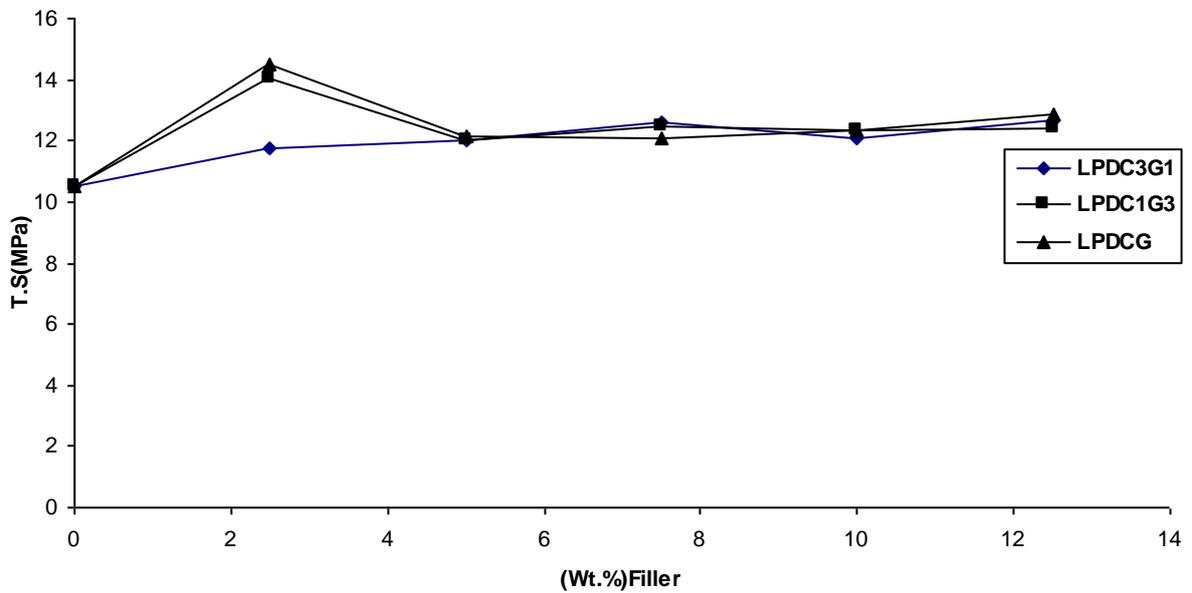


Fig.(۳-۵۷):Effect of fillers on the Tensile Strength of LDPE for [LPDCrG۱ , LPDCrG۲ , LPDCG] Polymers .

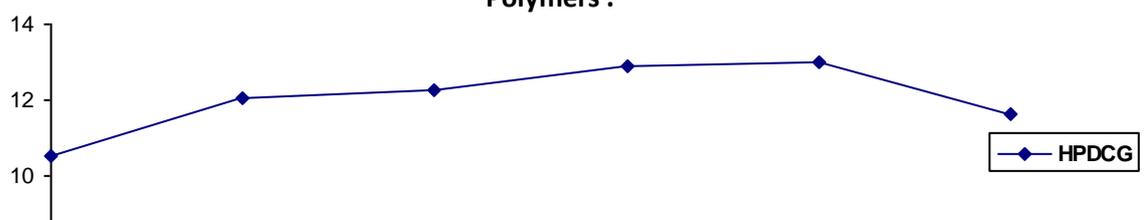


Fig.(3-8):Effect of fillers on the Tensile Strength of HDPE for [HPDCG] Polymers .

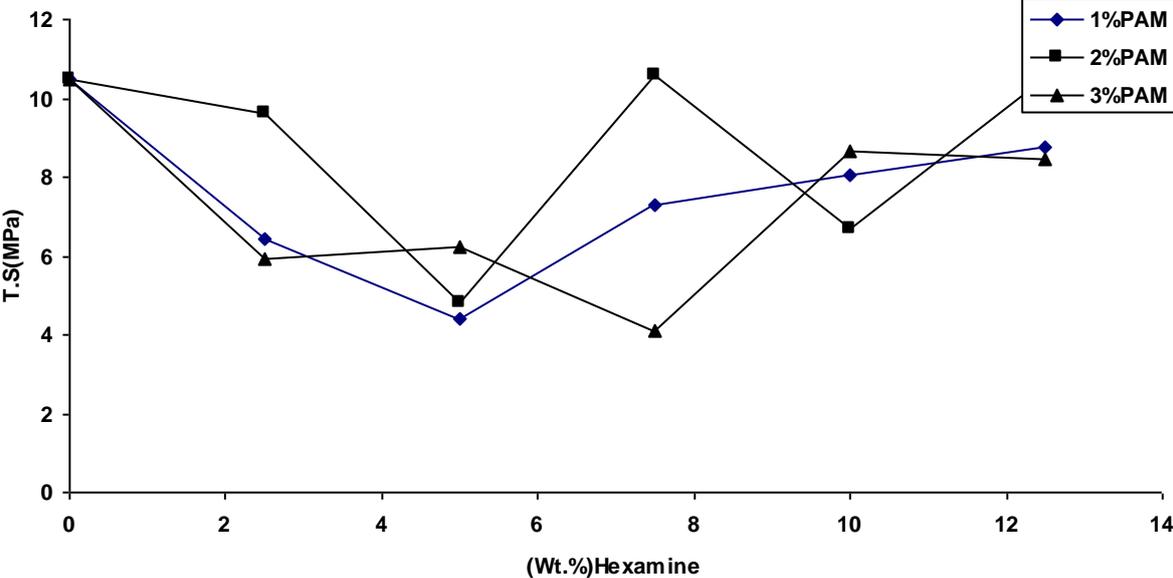


Fig.(۳-۵۹):Effect of hexamine on the Tensile Strength of LDPE for [LAM, HM , LAM, HM , LAM, HM] Polymers .

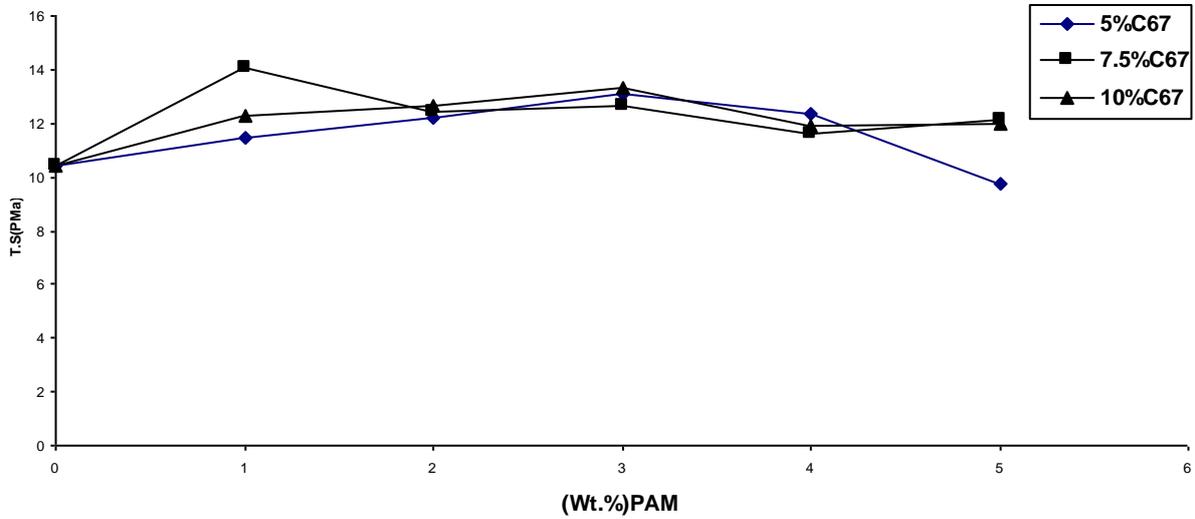


Fig.(۳-۶۰):Effect of PAM on the Tensile Strength of LDPE for [LAM, C۶۷ , LAM, C۶۷ , LAM, C۶۷] Polymers .

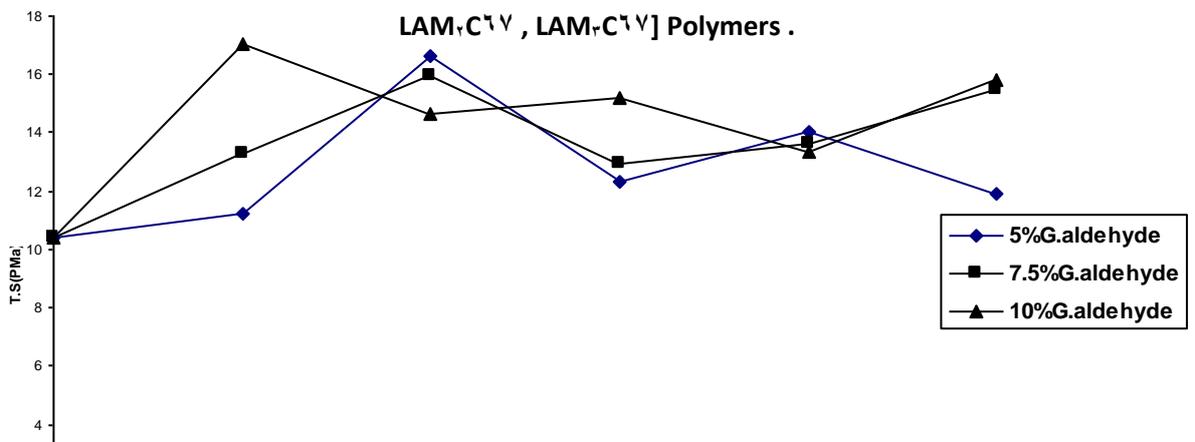


Fig.(۳-۶۱):Effect of PAM on the Tensile Strength of LDPE for[LAM_rGa ,
LAM_rGa , LAM_rGa] Polymers .

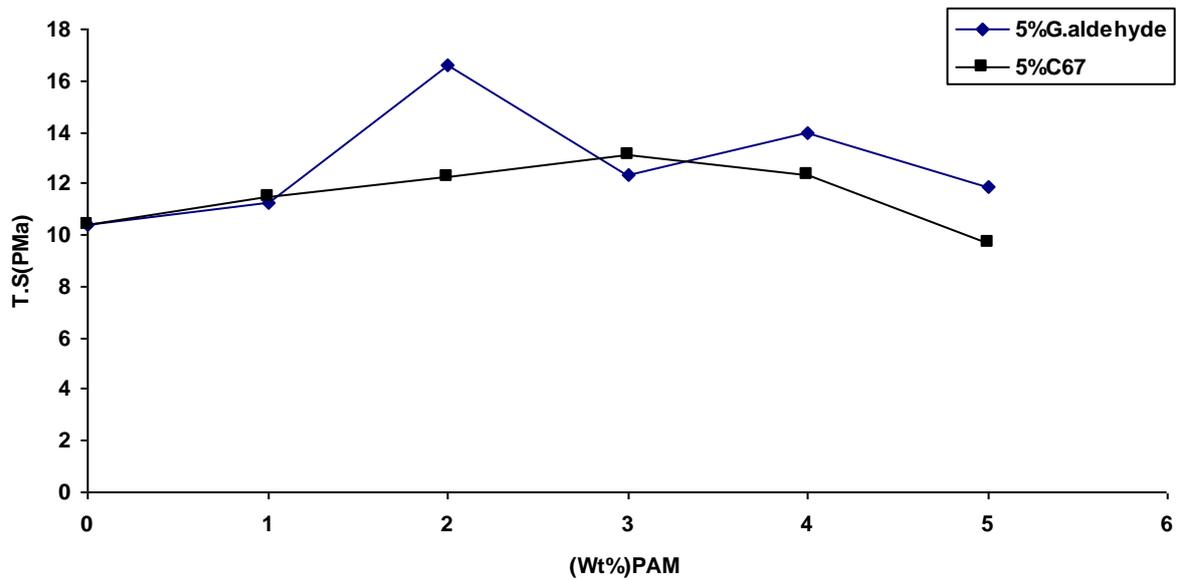


Fig.(3-62):Effect of PAM on the Tensile Strength of LDPE for
Polymers of (0% Ga , C_{1V}) .

[LAMGa , LAMC_{1V}]

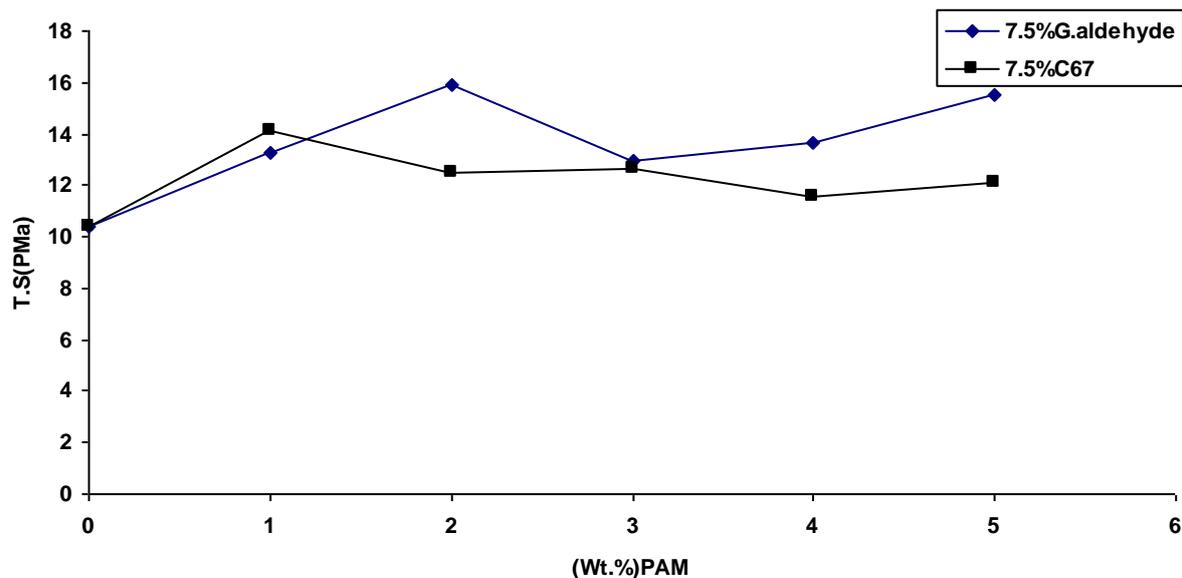


Fig.(3-63):Effect of PAM on the Tensile Strength of LDPE for
Polymers of (V.0% Ga , C_{1V}) .

[LAMGa , LAMC_{1V}]

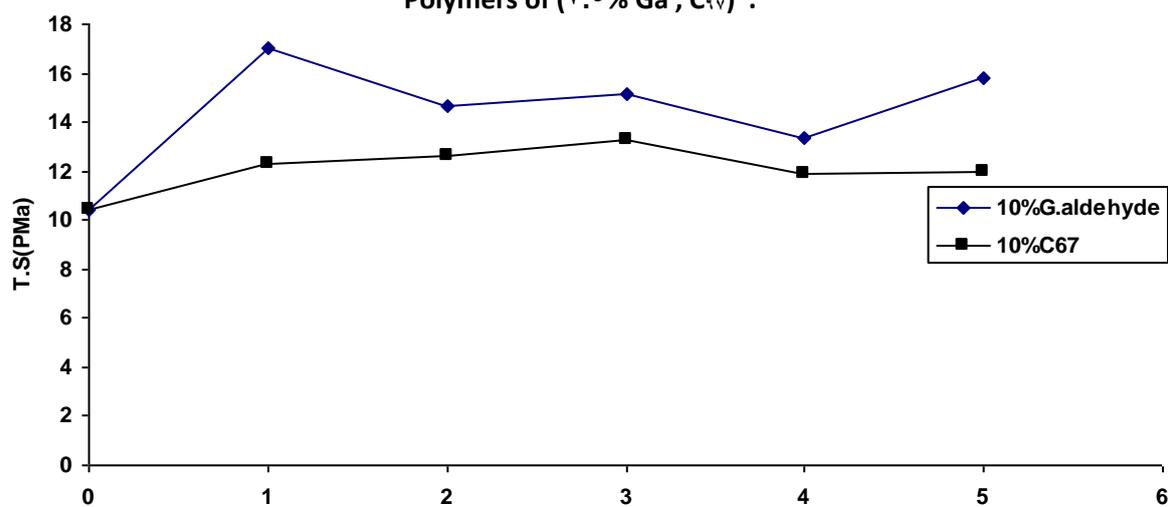


Fig.(3-64):Effect of PAM on the Tensile Strength of LDPE for
Polymers of (1.7% Ga, C₁₇) .

[LAMGa , LAMC₁₇]

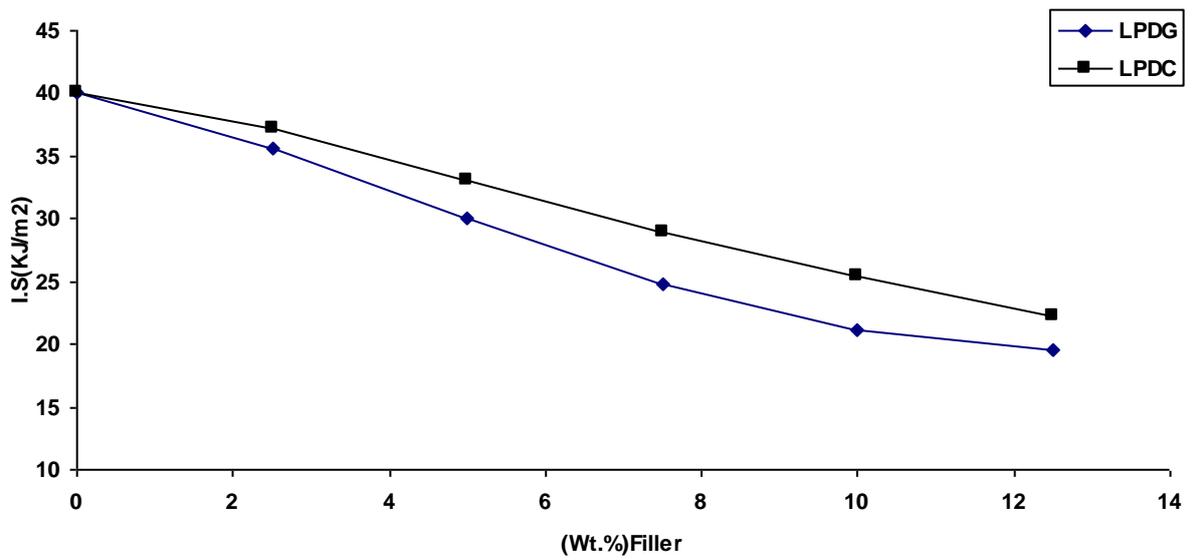


Fig.(3-65):Effect of fillers on the Impact Strength of LDPE for

[LPDG , LPDC] Polymers .

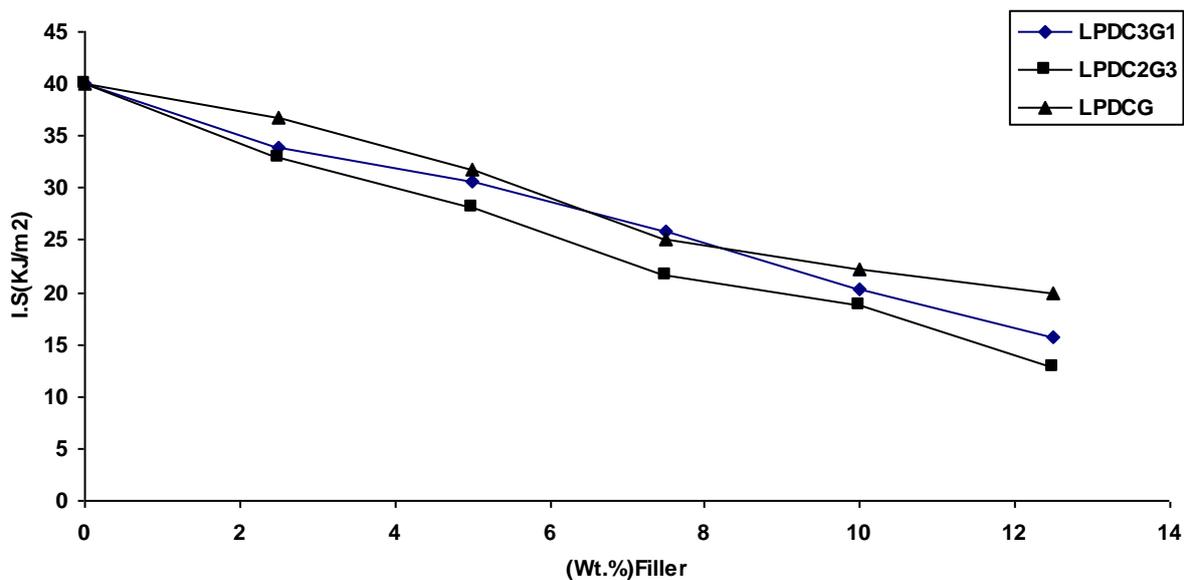


Fig.(۳-۶۶):Effect of mixed fillers (hybrid)on the Impact Strength of LDPE for

[LPDC_rG_۱ , LPDC_۱G_r , LPDCG] Polymers .

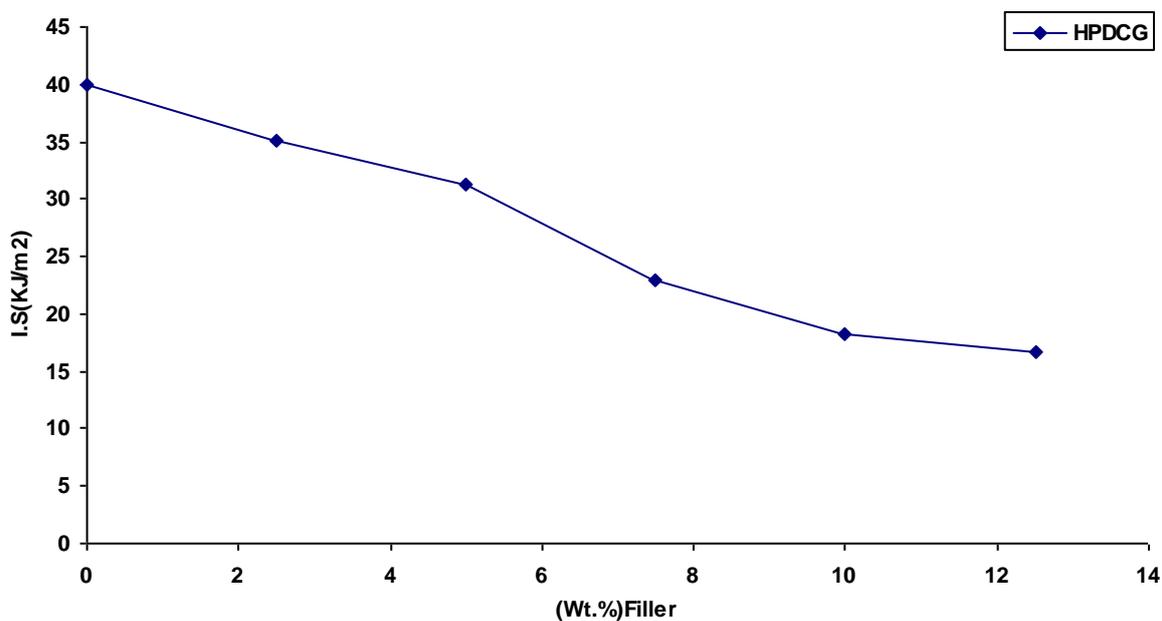


Fig.(3-17):Effect of mixed fillers on the Impact Strength of HDPE for [HPDCG] Polymers .

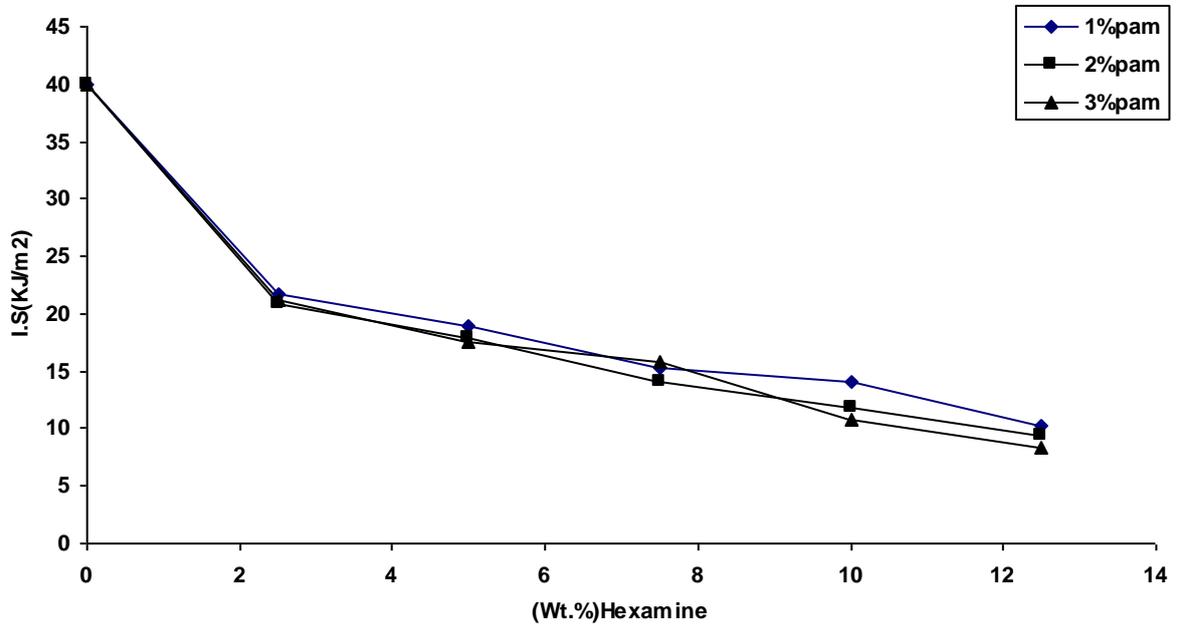


Fig.(3-18):Effect of hexamine on the Impact Strength of (LDPE with different ratio of PAM) for[LAM, HM , LAM+HM , LAM+HM] Polymers .

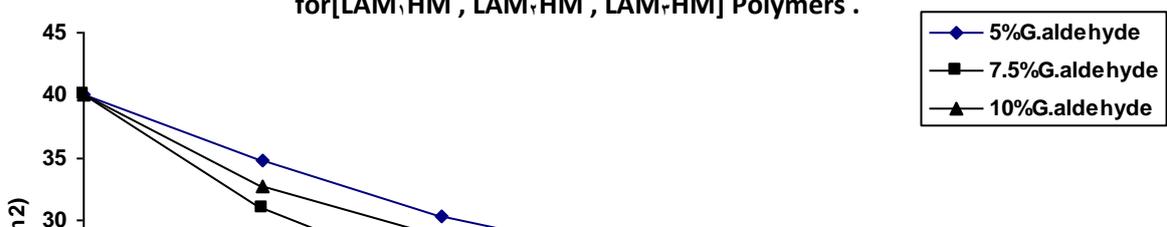


Fig.(۳-۶۹):Effect of PAM on the Impact Strength of (LDPE with different ratio of

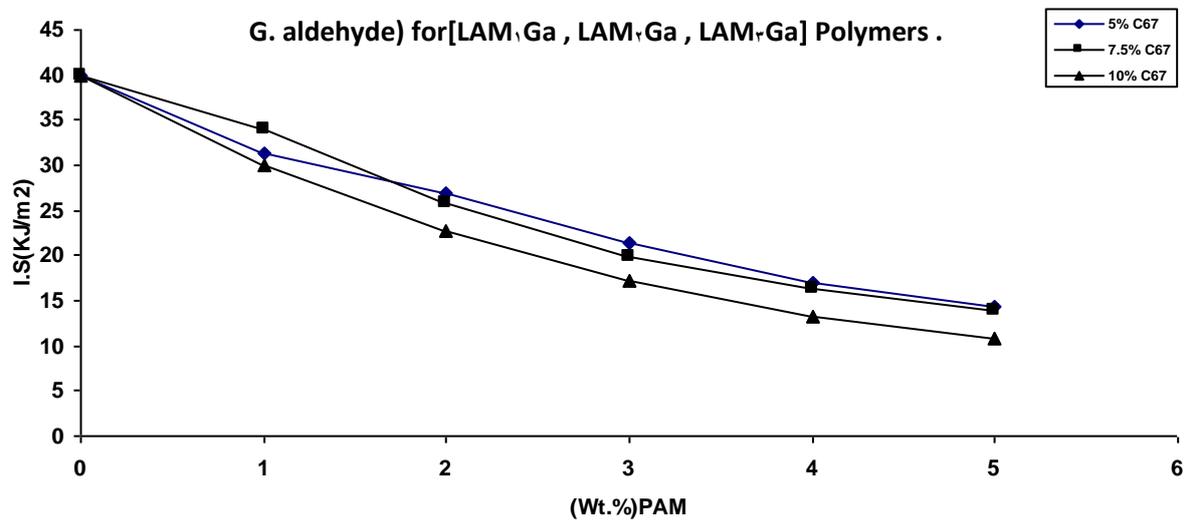


Fig.(3-70):Effect of PAM on the Impact Strength of (LDPE in the presence of peroxide C₆₇)for[LAM₁C₆₇ , LAM₂C₆₇ , LAM₃C₆₇] Polymers .

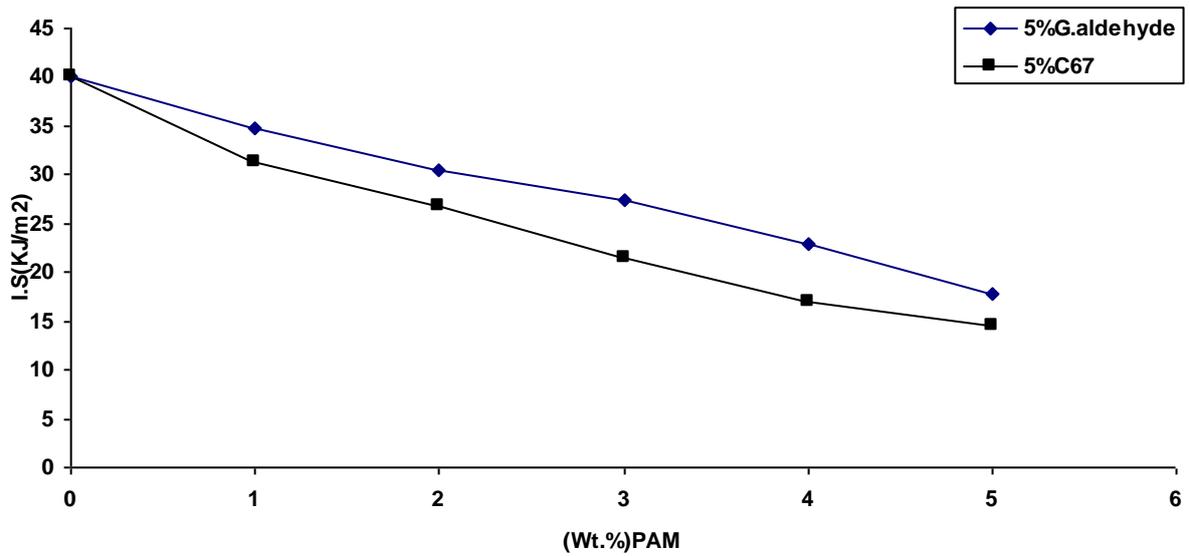


Fig.(3-71):Effect of PAM on the Impact Strength of LDPE for Polymers of (7.5% Ga , C₆₇) .

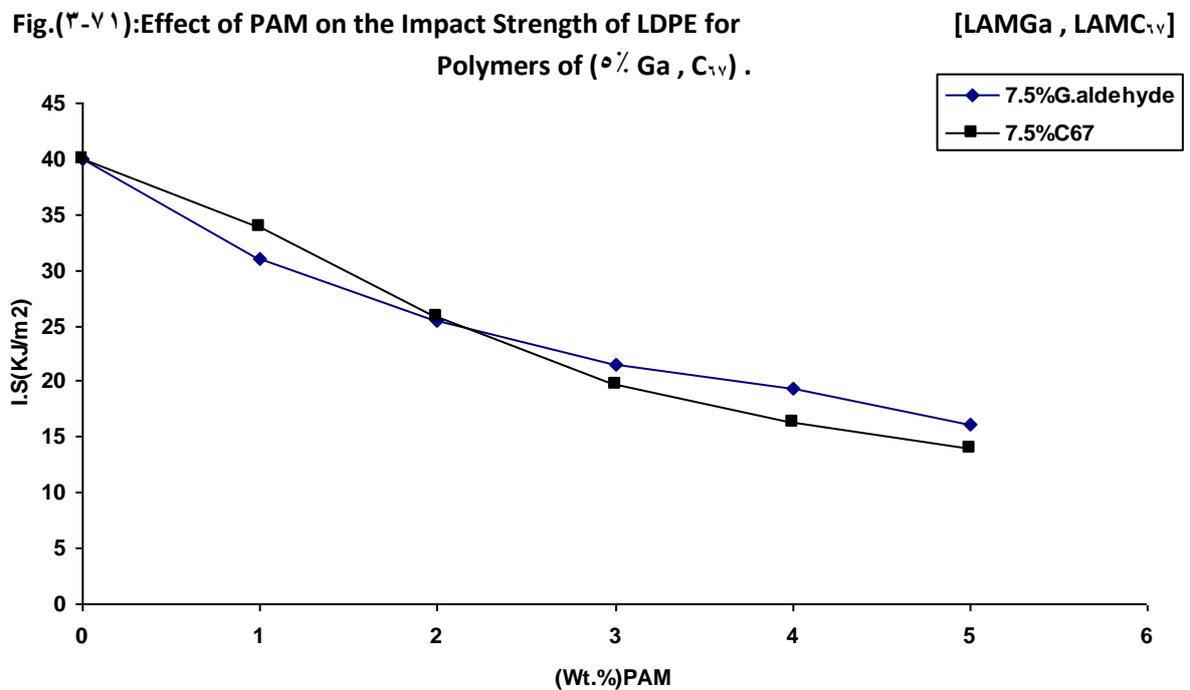


Fig.(۳-۷۲):Effect of PAM on the Impact Strength of LDPE for
Polymers of (۷.۵% Ga , C۱۷) .

[LAMGa , LAMC۱۷]

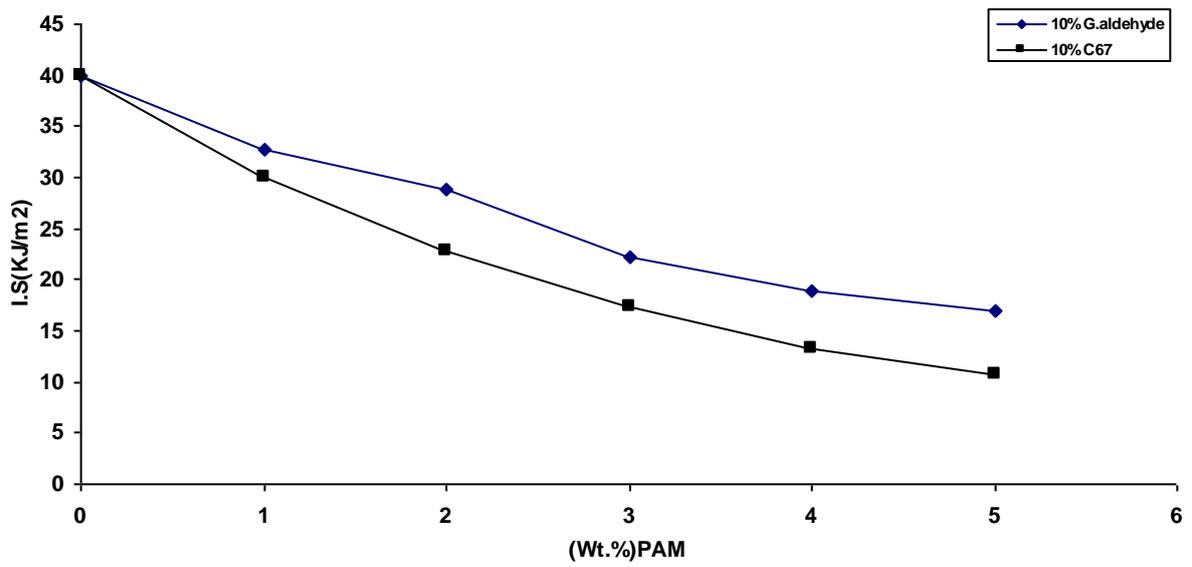


Fig.(3-13):Effect of PAM on the Impact Strength of LDPE for
 Polymers of (10% Ga, C10).

[LAMGa, LAMC10]

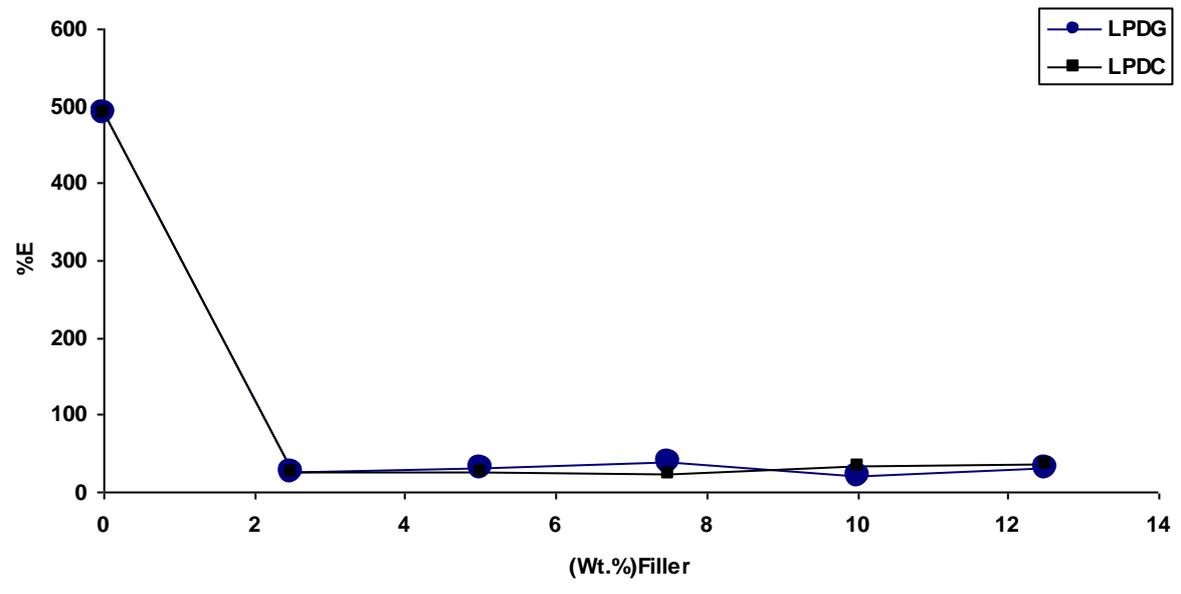


Fig.(3-14):Effect of fillers on the Elongation of LDPE for
 [LPDG, LPDC] Polymers .

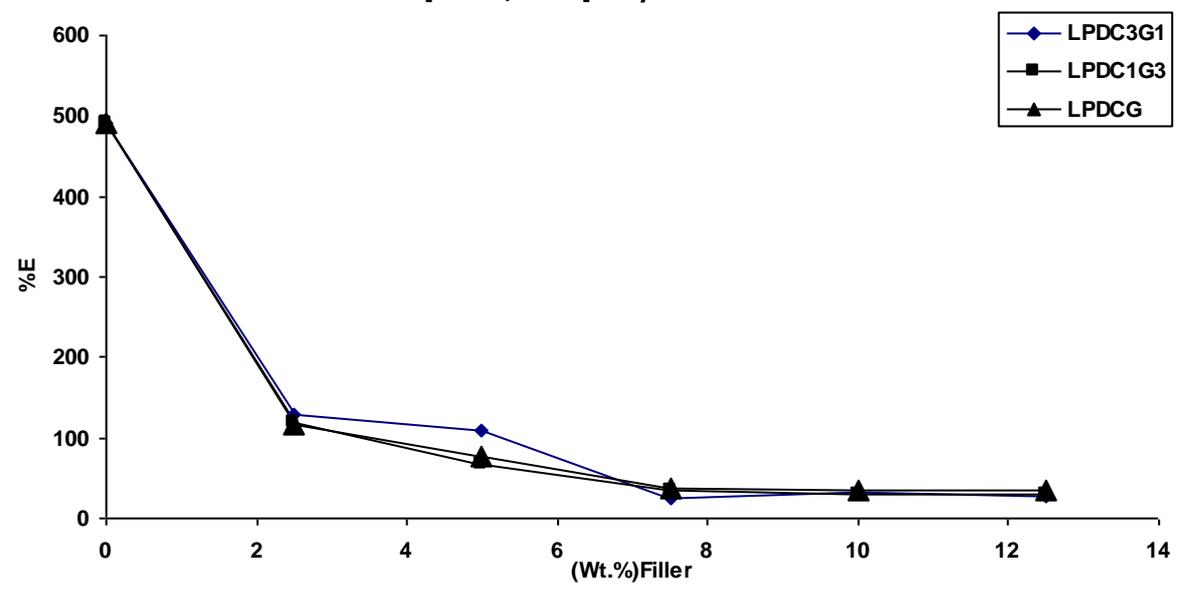


Fig.(3-70):Effect of mixed fillers (hybrid)on the Elongation of LDPE for [LPDCrG₁ , LPDC₁G_r , LPDCG] Polymers .

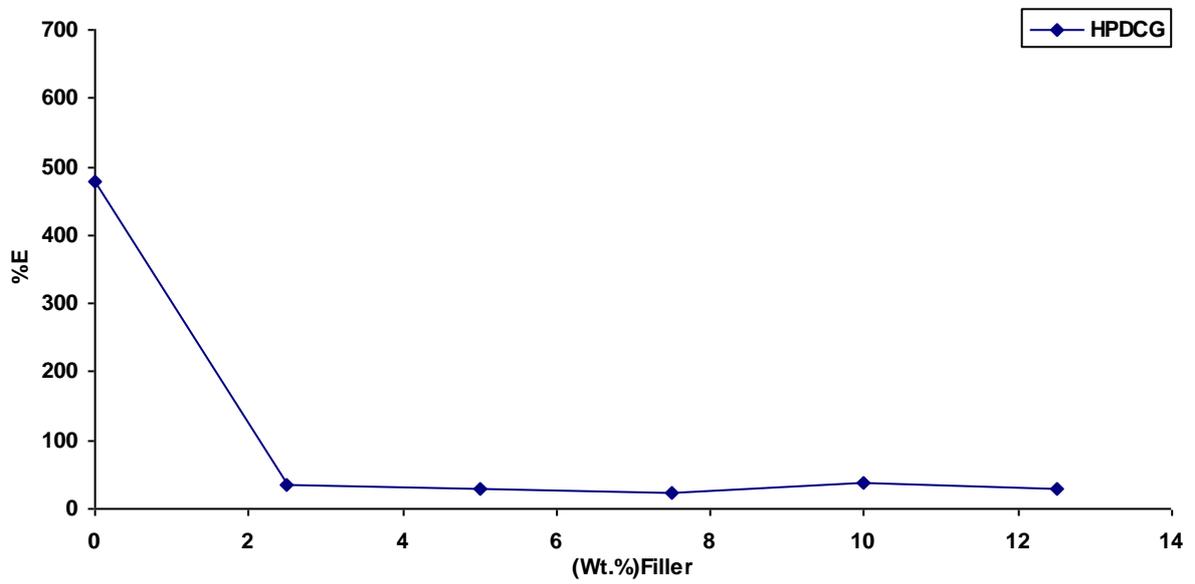


Fig.(3-71):Effect of mixed fillers on the Elongation of HDPE for [HPDCG] Polymers .



Fig.(3-11):Effect of hexamine on the Elongation of (LDPE with different ratio of PAM) for[LAM₁HM₁, LAM₁HM₂, LAM₁HM₃] Polymers .

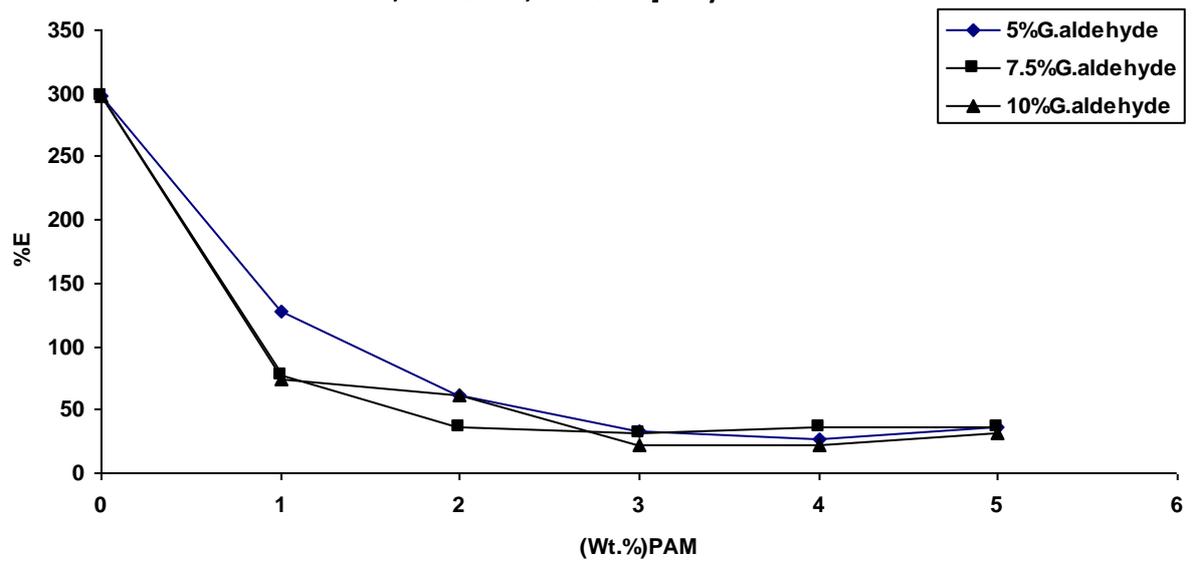


Fig.(3-7^):Effect of PAM on the Elongation of (LDPE with different ratio of

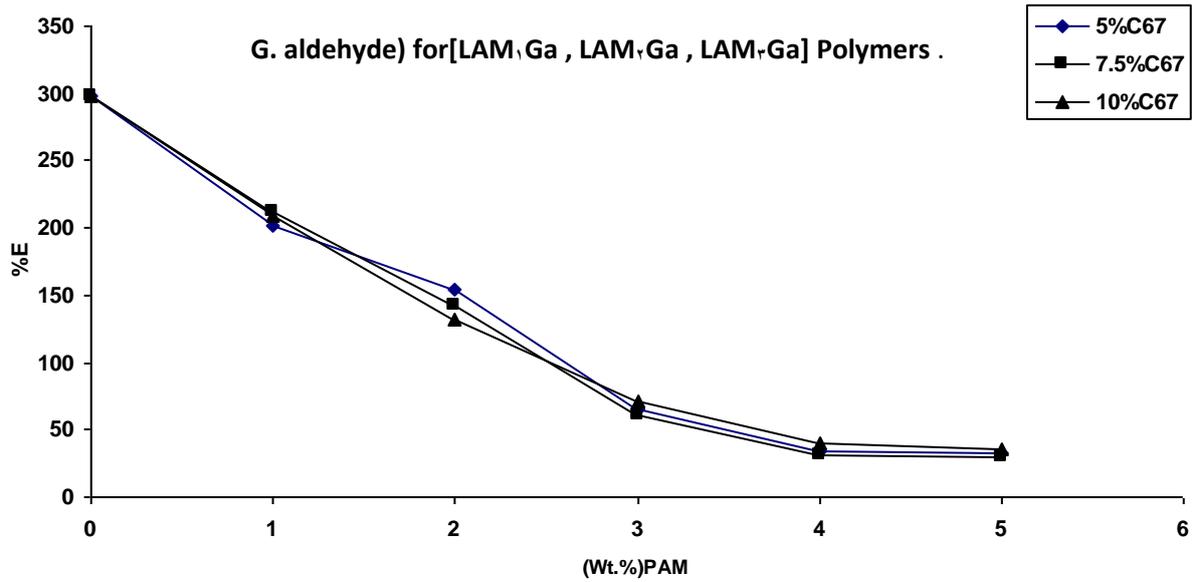


Fig.(3-7^):Effect of PAM on the Elongation of (LDPE in the presence of peroxide C₁₇)for[LAM₁C₁₇ , LAM₇C₁₇ , LAM_rC₁₇] Polymers .

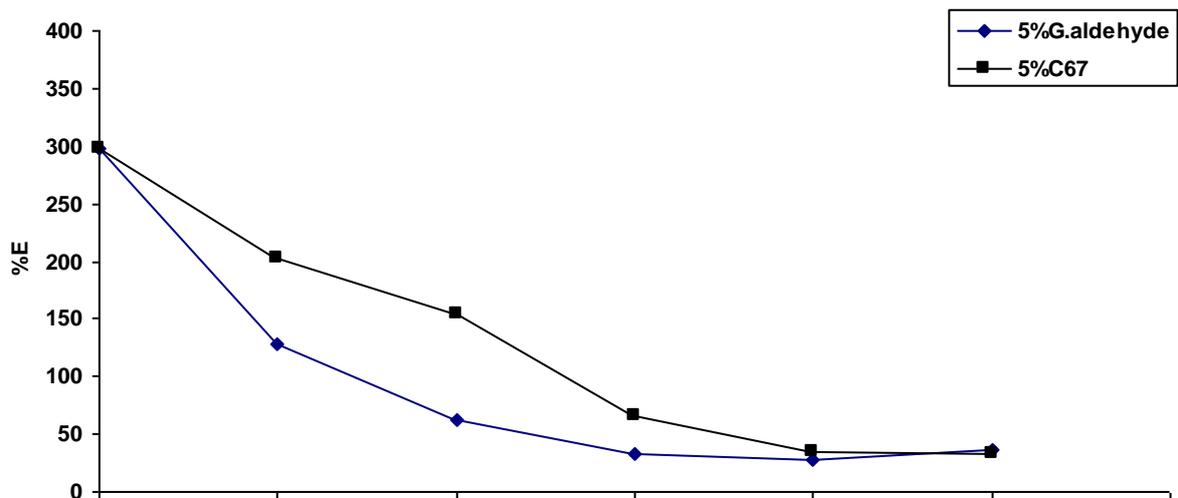


Fig.(3-10):Effect of PAM on the Elongation of LDPE for [LAMGa , LAMC_{1v}] Polymers of (5% Ga , C_{1v})

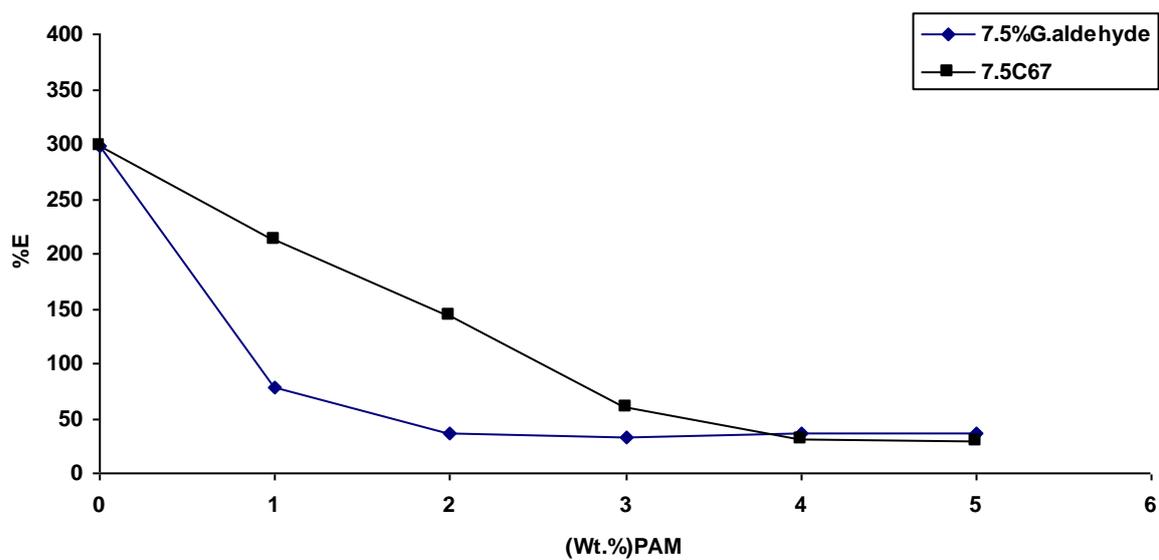


Fig.(3-11):Effect of PAM on the Elongation of LDPE for [LAMGa , LAMC_v] Polymers of (9.9% Ga , C_v) .

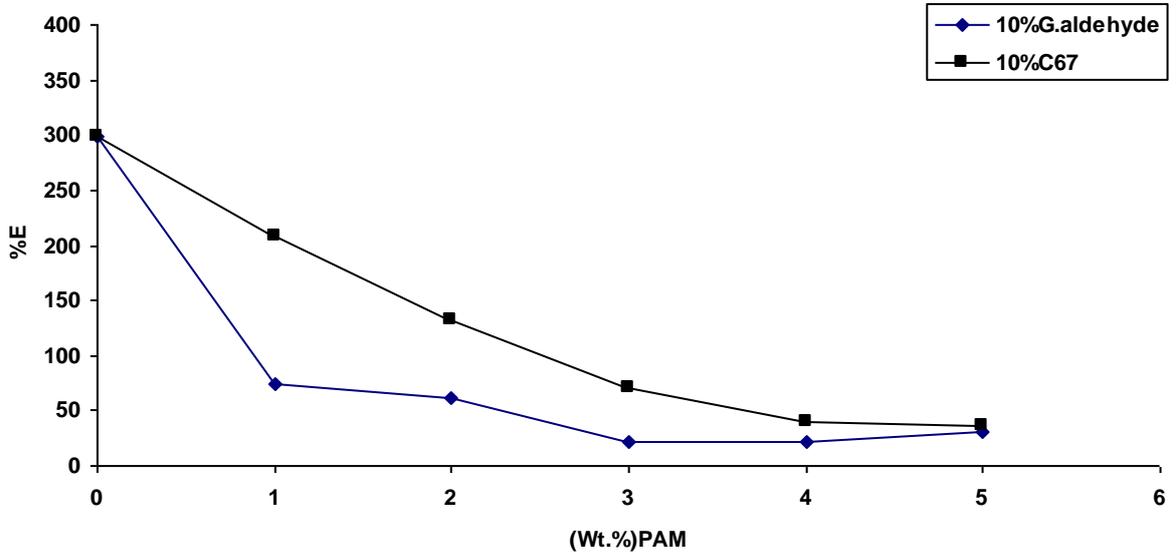


Fig.(3-12):Effect of PAM on the Elongation of LDPE for [LAMGa , LAMC_v] Polymers of (10% Ga , C_v) .

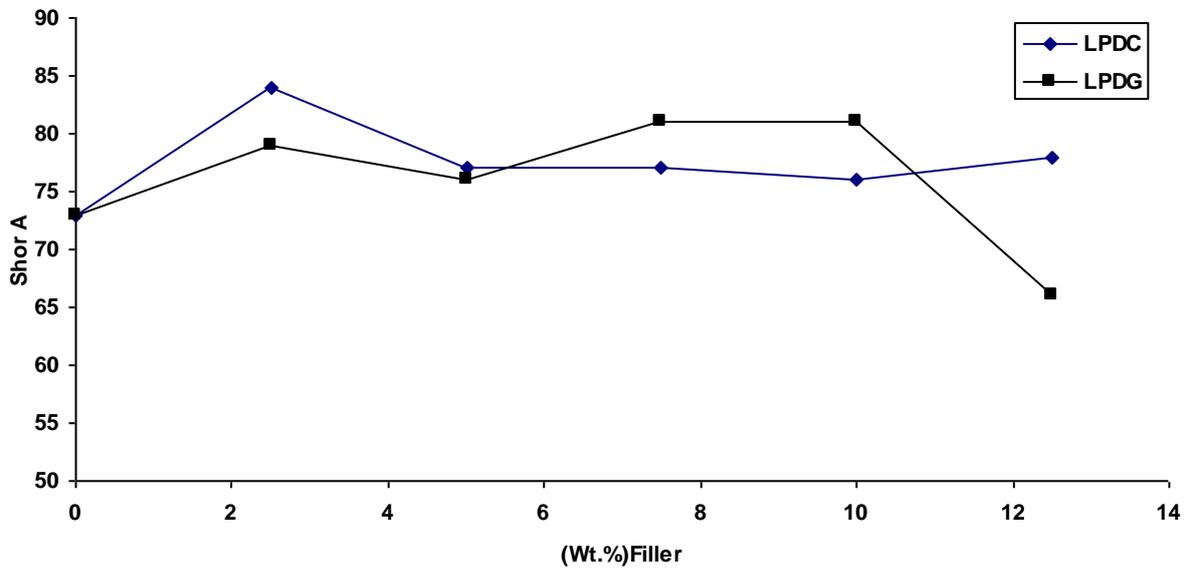


Fig.(3-13):Effect of fillers on the Hardness (Shor A) of LDPE for
[LPDG , LPDC] Polymers .

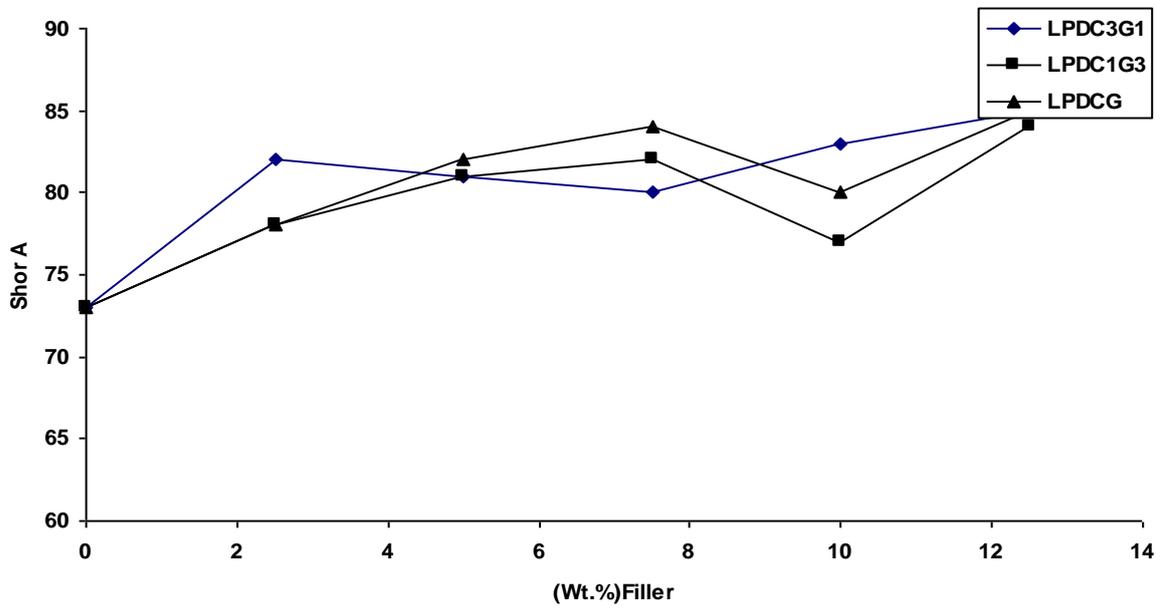


Fig.(3-14):Effect of mixed fillers (hybrid) on the Hardness (Shor A) of LDPE for
[LPDC_rG₁ , LPDC₁G_r , LPDCG] Polymers .

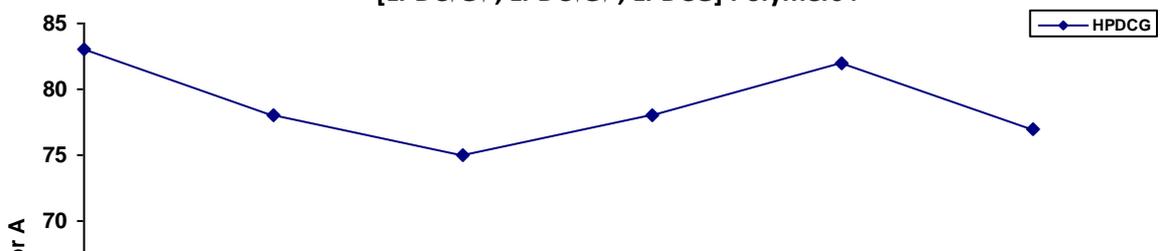


Fig.(3-8):Effect of mixed fillers on the Hardness (Shor A) of HDPE for [HPDCG] Polymers .

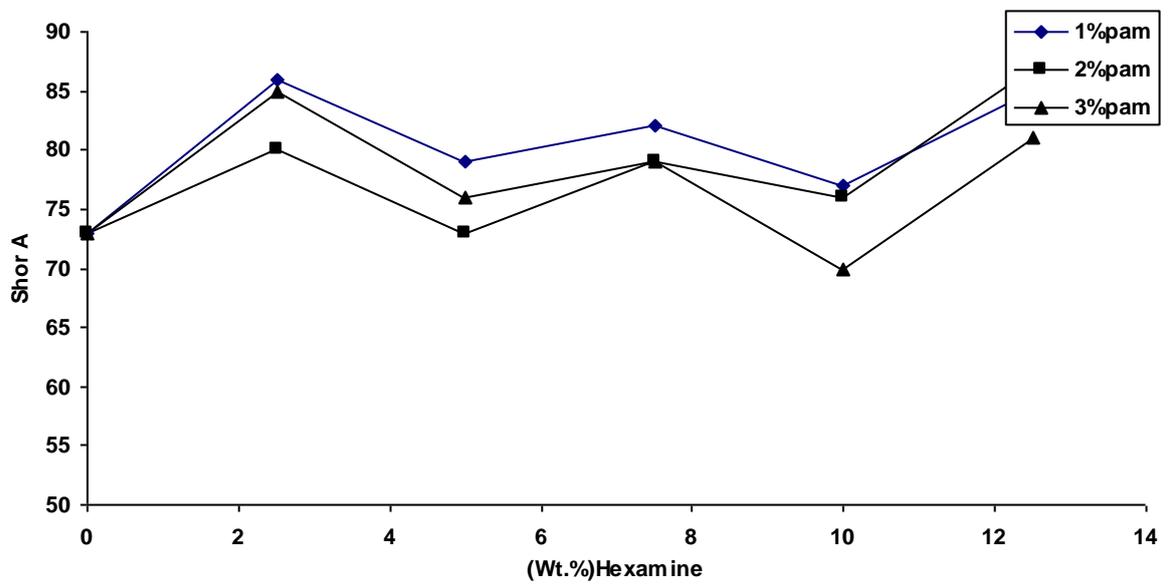


Fig.(3-86):Effect of hexamine on the Hardness (Shor A) of (LDPE with different ratio of PAM) for[LAM.HM , LAM_rHM , LAM_rHM] Polymers .

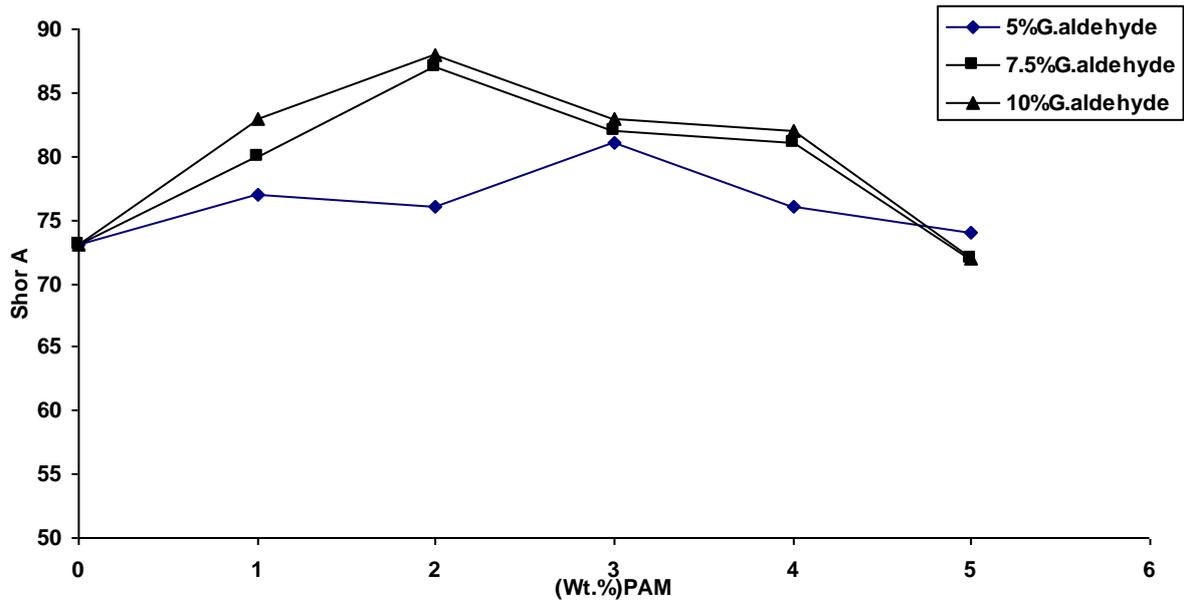


Fig.(3-87):Effect of PAM on the Hardness (Shor A)of (LDPE with different ratio of G. aldehyde) for[LAM.Ga , LAM_rGa , LAM_rGa] Polymers .

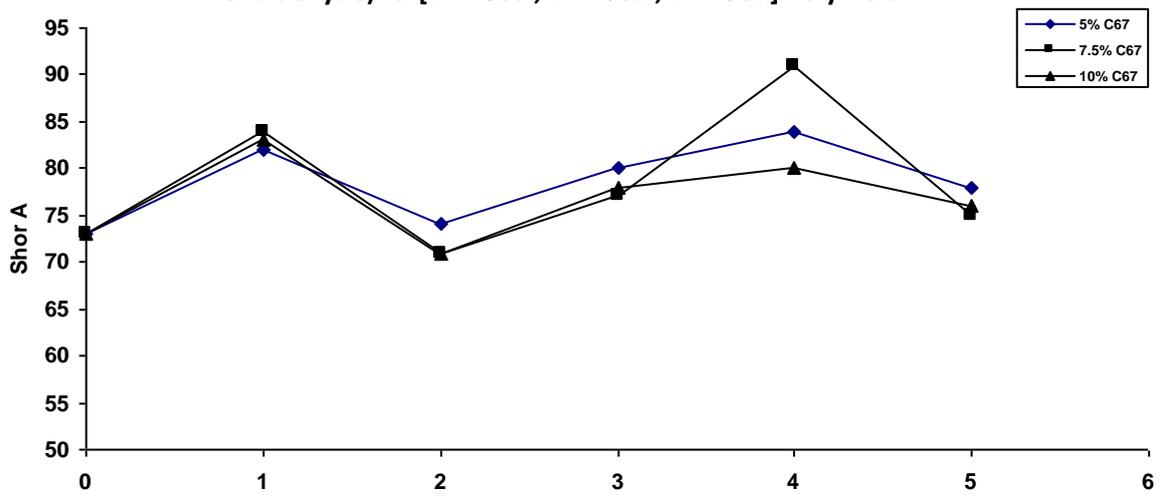


Fig. (3-11): Effect of PAM on the Hardness (Shor A) of (LDPE in the presence of peroxide C₆₇) for [LAM-C₆₇, LAM-C₆₇, LAM-C₆₇] Polymers .

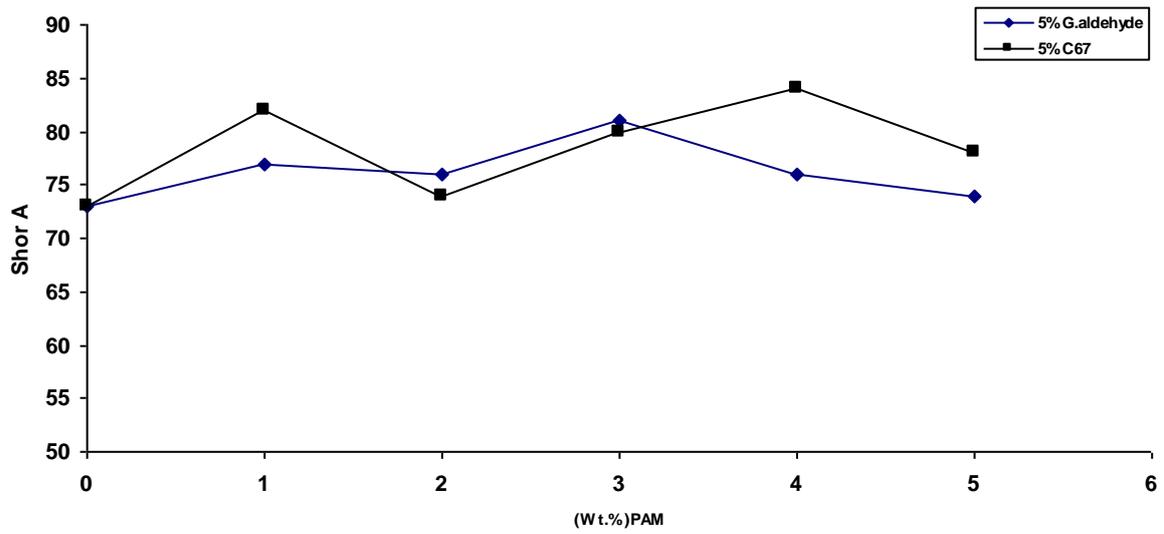


Fig.(3-89):Effect of PAM on the Hardness (Shor A)of LDPE for [LAMGa , LAMC_γ] Polymers of (0% Ga , C_γ) .

[LAMGa ,

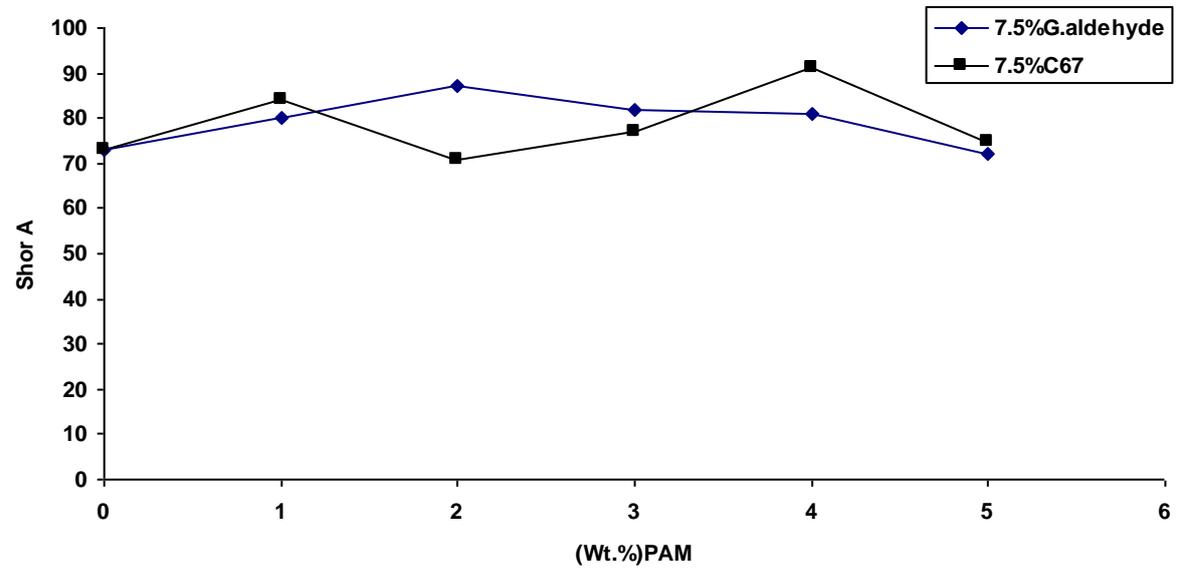


Fig.(3-90):Effect of PAM on the Hardness (Shor A)of LDPE for [LAMGa , LAMC_γ] Polymers of (10% Ga , C_γ) .

[LAMGa ,

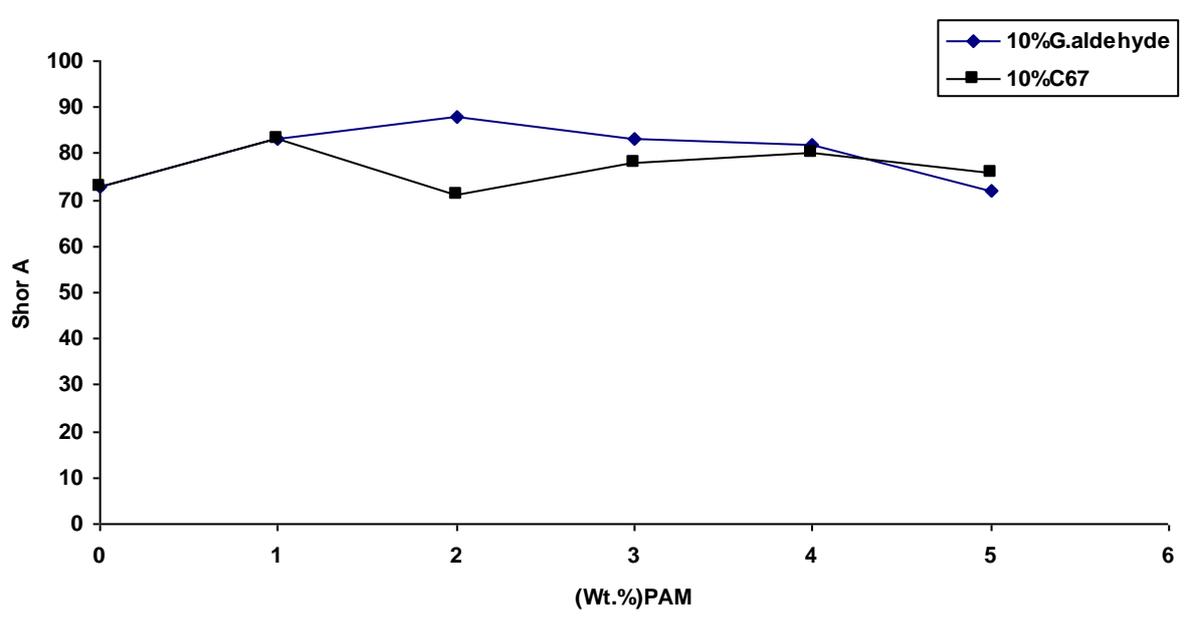


Fig.(3-91):Effect of PAM on the Hardness (Shor A)of LDPE for [LAMGa , LAMC_{1V}] Polymers of (1.0% Ga , C_{1V}) .

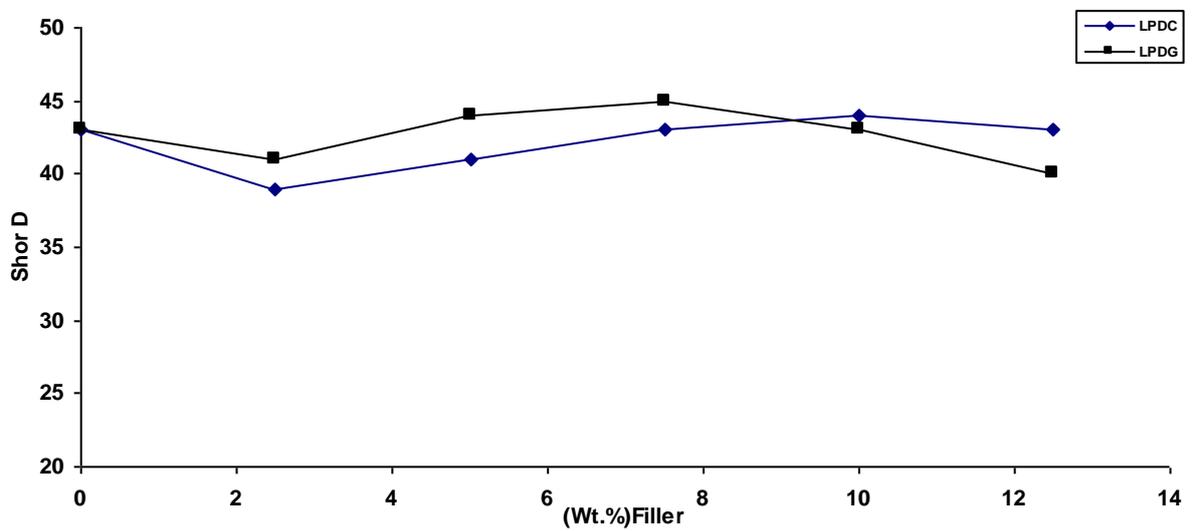


Fig.(3-92):Effect of fillers on the Hardness (Shor D) of LDPE for

[LPDG , LPDC] Polymers .

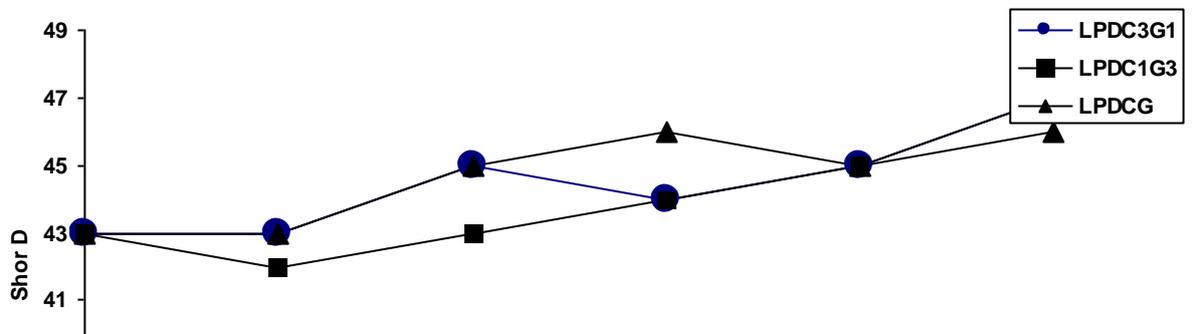


Fig.(۳-۹۳):Effect of mixed fillers (hybrid)on the Hardness (Shor D) of LDPE for
[LPDC_rG_۱ , LPDC_۱G_r , LPDCG] Polymers .

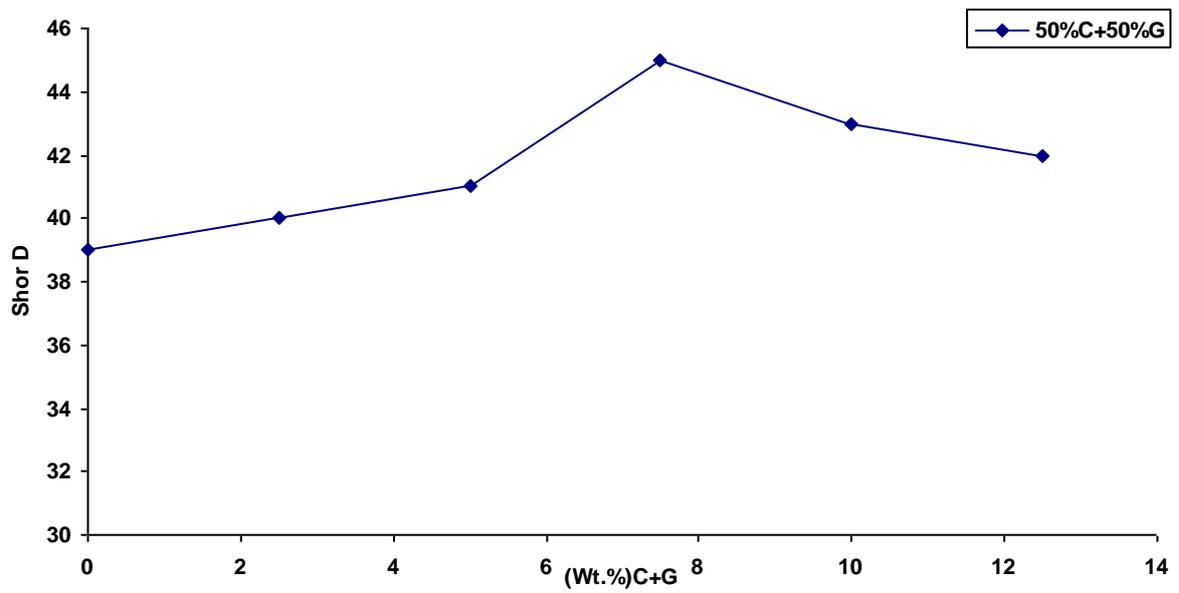


Fig.(۳-۹۴):Effect of mixed fillers on the Hardness (Shor D) of HDPE for [HPDCG] Polymers .

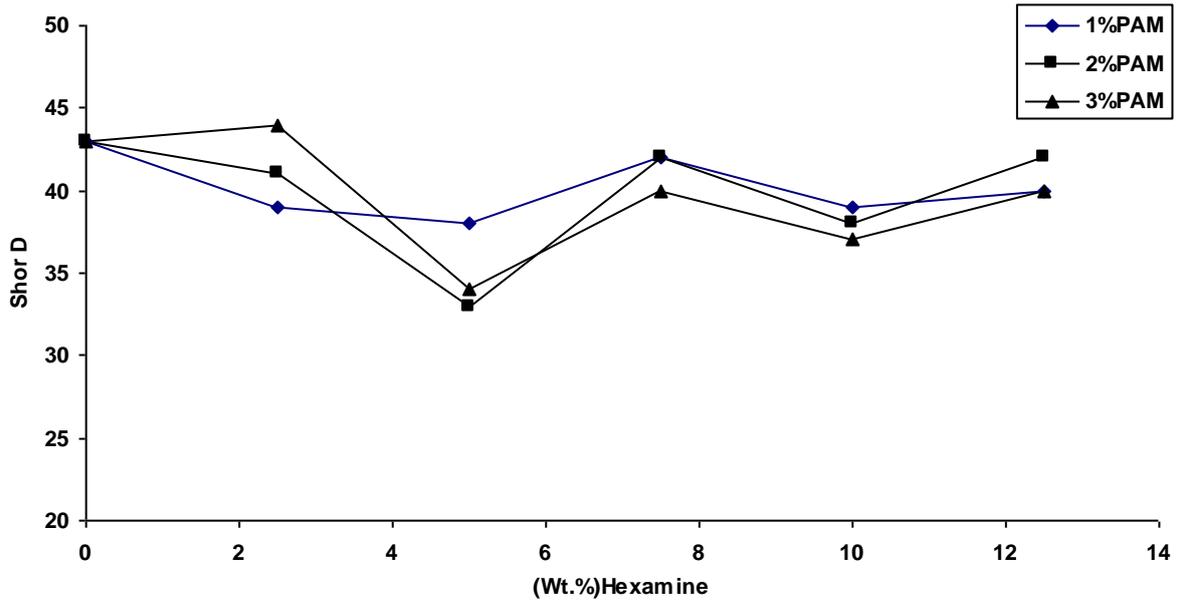


Fig.(۳-۹۵):Effect of hexamine on the Hardness (Shor D) of (LDPE with different ratio of PAM) for[LAM, HM , LAM, HM , LAM, HM] Polymers .

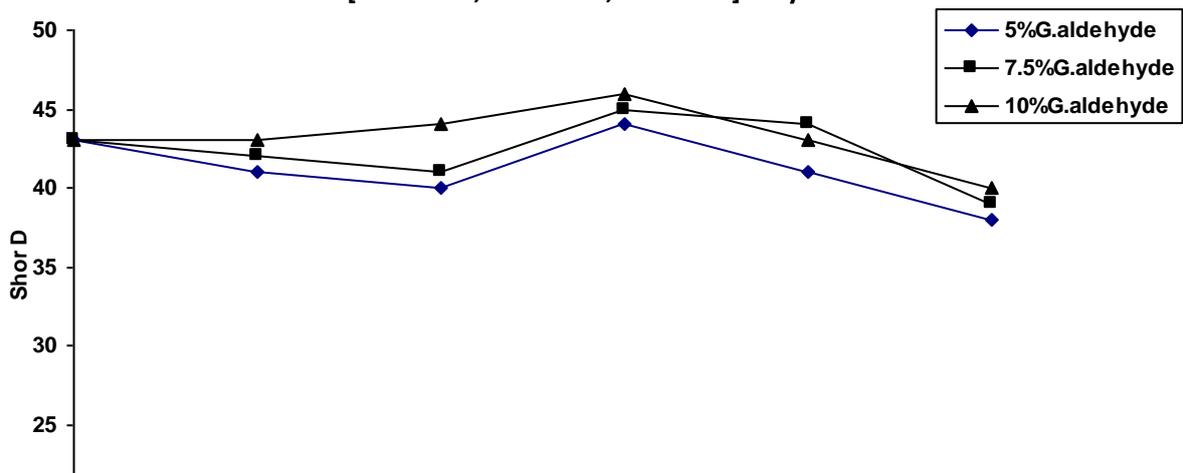


Fig.(۳-۹۶):Effect of PAM on the Hardness (Shor D)of (LDPE with different ratio of G. aldehyde) for[LAM₁Ga , LAM₇Ga , LAM₁₀Ga] Polymers .

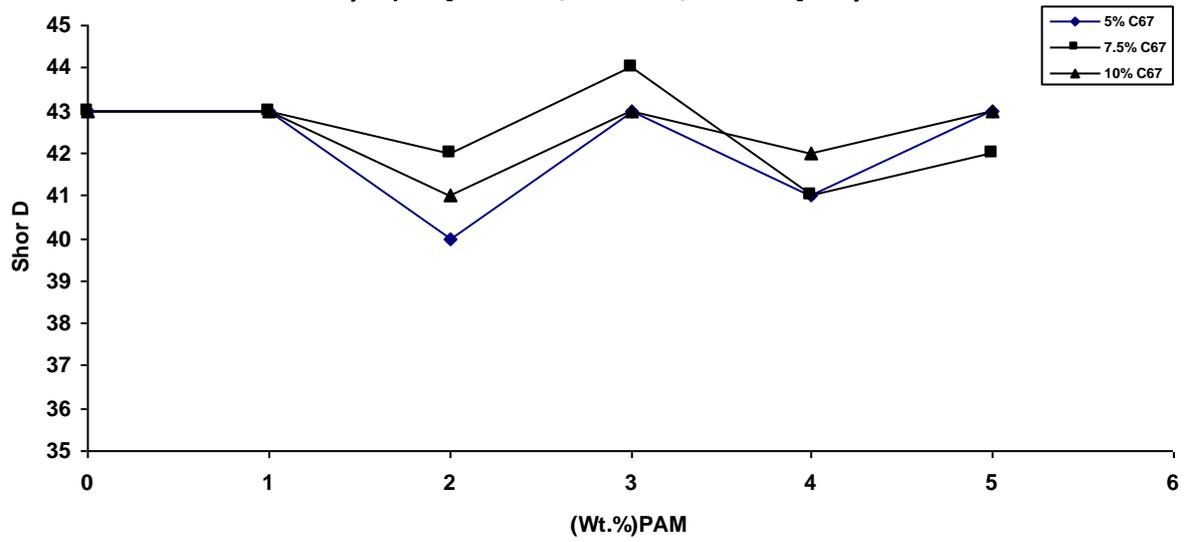


Fig.(3-97):Effect of PAM on the Hardness (Shor D)of (LDPE in the presence of peroxide C_{17})for[LAM C_{17} , LAM γC_{17} , LAM γC_{17}] Polymers .

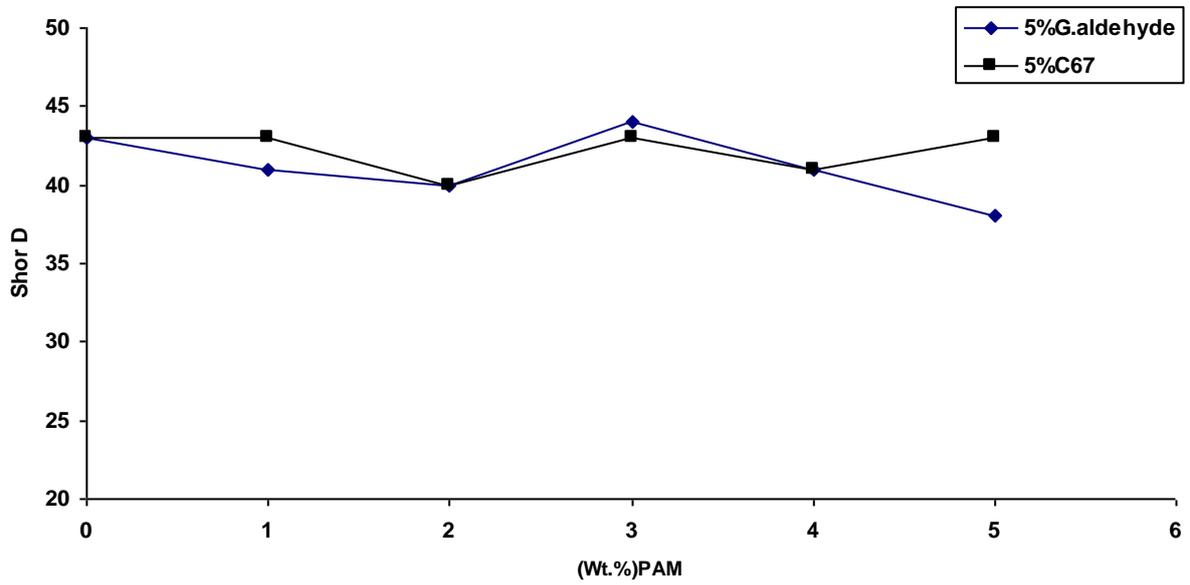


Fig.(3-98):Effect of PAM on the Hardness (Shor D)of LDPE for [LAMGa , LAM C_{17}] Polymers of (0% Ga , C_{17}) .

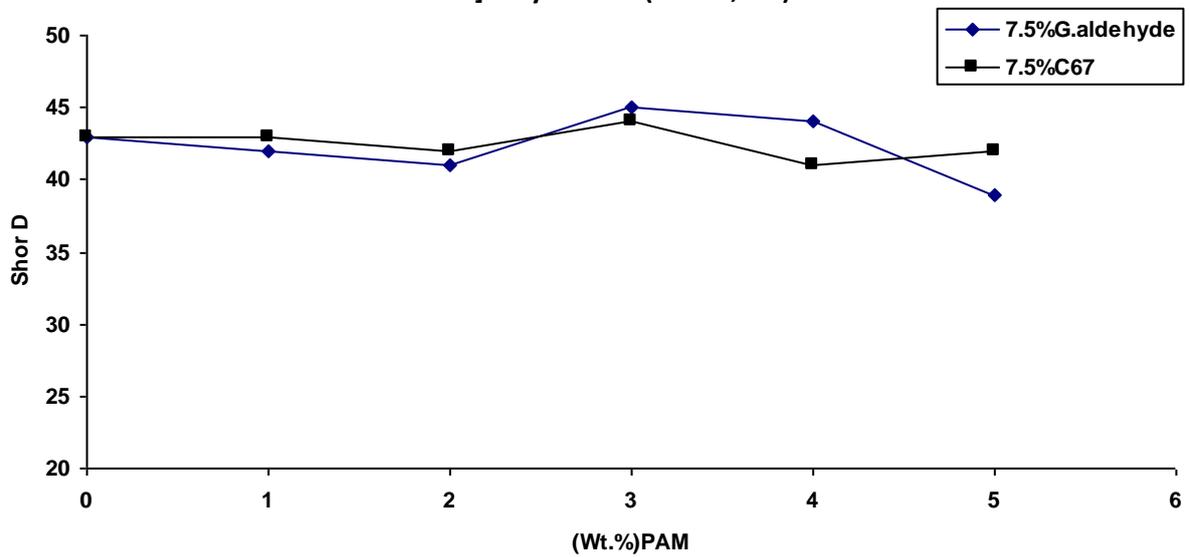


Fig.(3-99):Effect of PAM on the Hardness (Shor D)of LDPE for
LAMC_{1v}] Polymers of (V.0% Ga , C_{1v}) .

[LAMGa ,

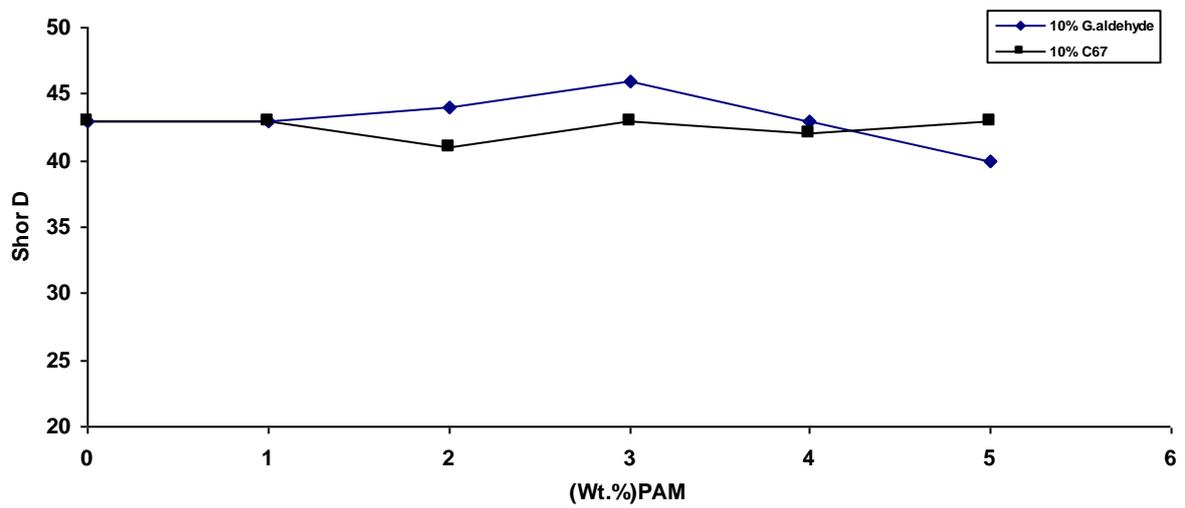


Fig.(3-100):Effect of PAM on the Hardness (Shor D)of LDPE for
LAMC_{1v}] Polymers of (1.0% Ga , C_{1v}) .

[LAMGa ,

۲-۳ Hydrigel Polymers

The gel is known for two compounds system non solution , when doing spread of low molecular weight through out the polymer chains cross linking . The cross linking between polymer molecules are divided for many types :

- ۱- The chemical bonds formed for cross linking reactions , when the polymer swelling in suitable polar solution . Gel formed when the cross linking's percentage is lower .
- ۲- The intermolecular bonds , when its strong enough to resist interference energy between polymer and solvent .
- ۳- The bonds formed between ions in the solutions and polar groups of polymer .
- ۴- The bonds formed between the polymer chains and additives particles (fillers) has active spreads property between solution molecules .

The gel differ from solution , where the gel is insoluble due to the bonds between chains or due to top molecules compounds which prevent bonds movement . When making gels medium between solution state and solid state .

3-3-1 Swelling and deswelling studies as a function of time

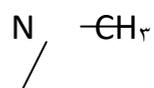
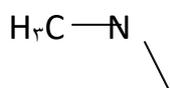
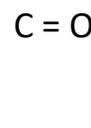
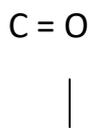
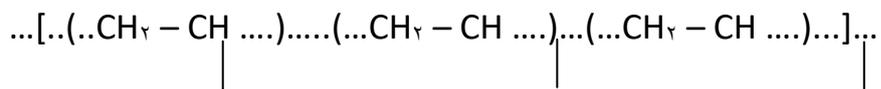
The swelling ratio (Q) as a function of time at room temperature of the prepared hydrogel [LPEHM] is shown in Fig.(3-1.1) . It is clear that the swelling ratio (Q) is increased with the increase of adding polyelectrolyte up to concentration of (0% w/w) . An increase in polyelectrolyte concentration from (2 – 0% w/w) will increased the swelling ratio (Q) twice . The above swelling behavior is due to the decrease of cross linking density (i.e large free volume), this conclusion is similar to that found by R. Weast⁽¹⁴⁾ .

The deswelling rate of the hydrogel [LPEHM] is shown in

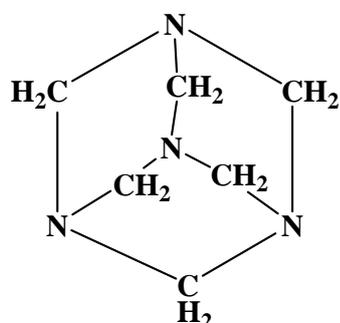
Fig.(3-1.2) . It clearly that the water loss cellulite as the percentage (w/w) is large with the decreasing of cross linking . At time (0 hrs) the

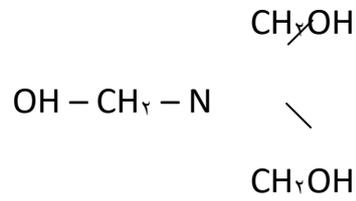
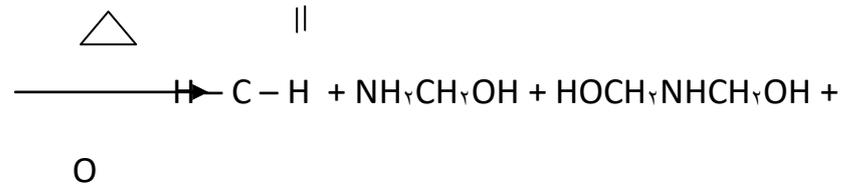
(0% polyelectrolyte) will loss about (22.2%) . All type of hydrogel were dried (i.e loss all water of at ≈ 3 hrs) .

The cross linking of hexamine (HM) with polyethylene and polyelectrolyte may be represented as follows :

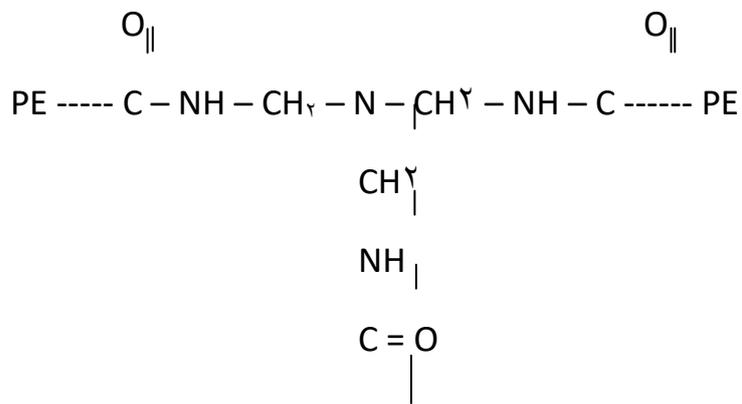
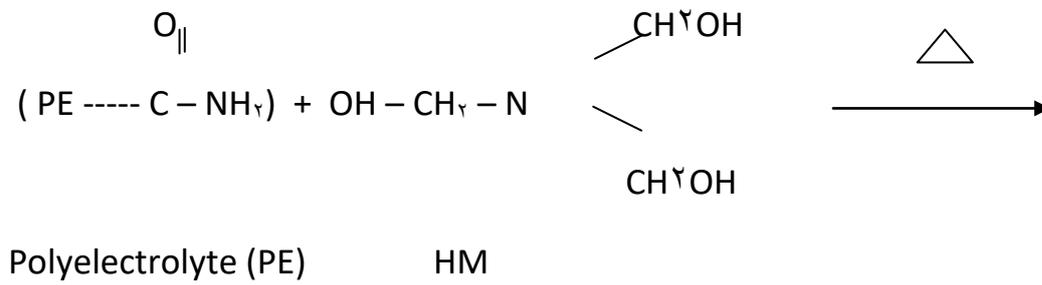


Polyelectrolyte (PE ----- C - NH_r)





Hexamine (HM)

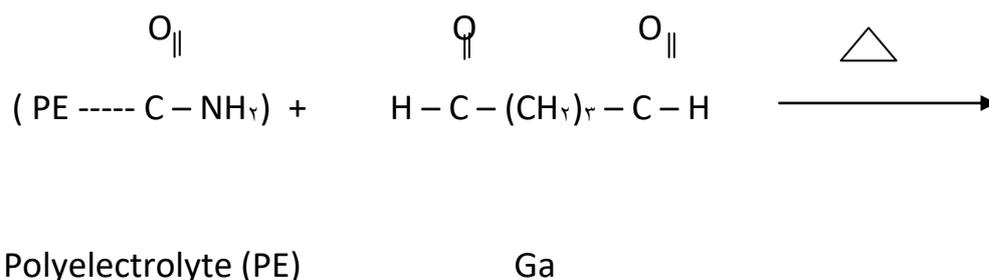


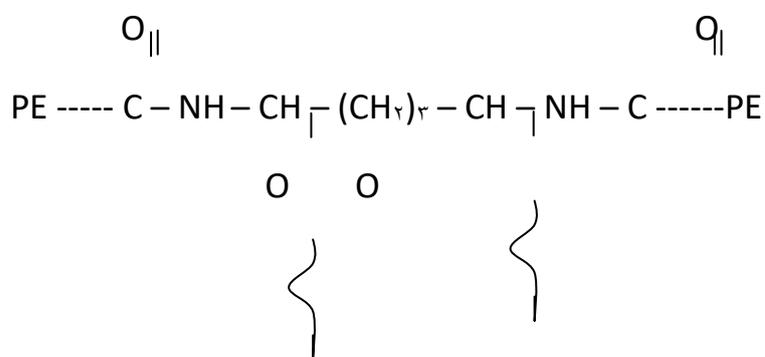
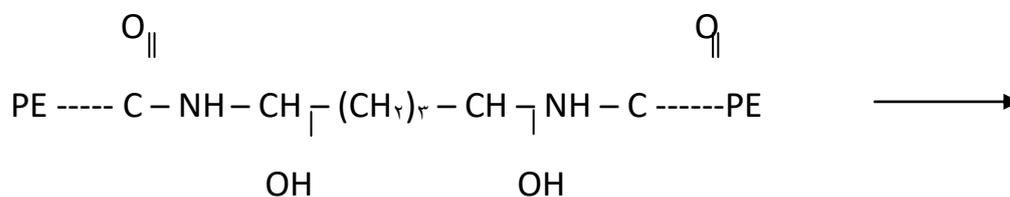
PE

The swelling ratio (Q) as a function of time at room temperature of the prepared hydrogel [LPEGa] is shown in Fig.(3-1.3) . It is clear that the swelling ratio (Q) is increased with the increase of adding polyelectrolyte up to concentration of (0% w/w) . An increase in polyelectrolyte concentration from (1 – 0% w/w) will increased the swelling ratio (Q) twice . The above swelling behavior is due to the decrease of cross linking density (i.e large free volume), this conclusion is similar to that found by T. Jahns⁽²⁶⁾ .

The deswelling rate of the hydrogel [LPEGa] is shown in Fig.(3-1.4) . It clearly that the water loss cellulite as the percentage (w/w) is large with the decreasing of cross linking . At time (0 hrs) the (0% polyelectrolyte) will loss about (17.9%) . All type of hydrogel were dried (i.e loss all water of at 24 hrs) .

The cross linking of gluteraldehyde (Ga) with polyethylene and polyelectrolyte may be represented as follows :





The swelling ratio (Q) as a function of time at room temperature of the prepared hydrogel [LPEC_x] is shown in Fig.(3-10) . It is clear that the swelling ratio (Q) is increased with the increase of adding polyelectrolyte up to concentration of (0% w/w) . An increase in polyelectrolyte concentration from (1 - 0% w/w) will increased the swelling ratio (Q) twice . The above

swelling behavior is due to the decrease of cross linking density (i.e large free volume), this conclusion is similar to that found by G. Rathna⁽²⁶⁾.

The deswelling rate of the hydrogel [LPEC_{1v}] is shown in

Fig.(3-1,6) . It clearly that the water loss cellulite as the percentage (w/w) is large with the decreasing of cross linking . At time (0 hrs) the

(0% polyelectrolyte) will loss about (22.7%) . All type of hydrogel were dried (i.e loss all water of at 24 hrs) .

The cross linking of peroxide (C_{1v}) with polyethylene and polyelectrolyte may be represented as follows :

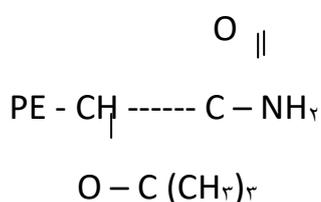
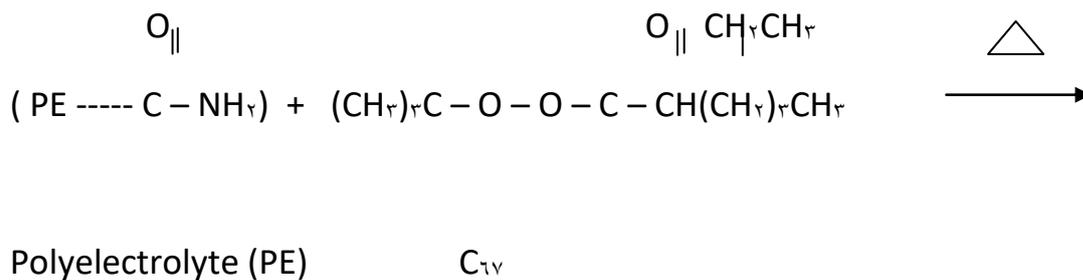


Fig.(3-1.7) show comparison of using different cross linking agent at fixed concentration (1% w/w). The figure clearly shown that uptake water follows the order . Peroxide (C_{1v}) (0.190) > Hexamine (HM) (0.180) > Gluteraldehyde (Ga) (0.093) . This behavior may be due to the variation in the cross linking density of the hydrogel⁽²⁶⁷⁻²⁶⁸⁾ .

The rate of losing water for the above three types of cross linking were Hexamine (HM) > Peroxide (C_{1v}) > Gluteraldehyde (Ga) as shown in Fig.(3-1.8) . Gluteraldehyde (Ga) deswelling was so slowly that it dried after 10 hrs. This is due to large free volume size⁽²⁶⁴⁾ .

Fig.(3-1.9) show comparison of using different cross linking agent at fixed concentration (2% w/w) . The figure clearly shown that uptake water

follows the order .Peroxide(C_{1v})(0.09) > Gluteraldehyde (Ga) (0.24) > Hexamine (HM) (0.18) . This behavior may be due to the variation in the cross linking density of the hydrogel⁽²⁶⁷⁻²⁶⁸⁾ .

The rate of losing water for the above three types of cross linking were Peroxide (C_{1v}) > Hexamine (HM) > Gluteraldehyde (Ga) as shown in Fig.(3-11) . Gluteraldehyde (Ga) deswelling was so slowly that it dried after 32 hrs. This is due to large free volume size⁽²⁶⁴⁾ .

Fig.(3-11) show comparison of using different cross linking agent at fixed concentration (3% w/w) . The figure clearly shown that uptake water follows the order .Peroxide(C_{1v})(0.10) > Gluteraldehyde (Ga) (0.001) > Hexamine (HM) (0.23) . This behavior may be due to the variation in the cross linking density of the hydrogel⁽²⁶⁷⁻²⁶⁸⁾ .

The rate of losing water for the above three types of cross linking were Peroxide (C_{1v}) > Hexamine (HM) > Gluteraldehyde (Ga) as shown in Fig.(3-112) . Gluteraldehyde (Ga) deswelling was so slowly that it dried after 31 hrs. This is due to large free volume size⁽²⁶⁴⁾ .

Fig.(3-113) show comparison of using different cross linking agent at fixed concentration (4% w/w) . The figure clearly shown that uptake water follows the order . Gluteraldehyde (Ga) (0.703) > Peroxide (C_{1v})(0.640) > Hexamine (HM) (0.318) . This behavior may be due to the variation in the cross linking density of the hydrogel⁽²⁶⁷⁻²⁶⁸⁾ .

The rate of losing water for the above three types of cross linking were Peroxide (C_{1v}) ≈ Hexamine (HM) ≈ Gluteraldehyde (Ga) as shown in Fig.(3-114)⁽²⁶⁶⁾ .

Fig.(3-110) show comparison of using different cross linking agent at fixed concentration (0% w/w). The figure clearly shown that uptake water follows the order . Gluteraldehyde (Ga) (0.901) > Peroxide (C_{1v}) (0.719) > Hexamine (HM) (0.379) . This behavior may be due to the variation in the cross linking density of the hydrogel ⁽²⁶⁷⁻²⁶⁸⁾ .

The rate of losing water for the above three types of cross linking were Peroxide (C_{1v}) \approx Hexamine (HM) > Gluteraldehyde (Ga) as shown in Fig.(3-116) Gluteraldehyde (Ga) deswelling was so slowly that it dried after 0. hrs. This is due to large free volume size ⁽²⁶⁶⁾ .

٣-٣-٢ IR Spectra

Fig.(٣-١٢) show the FTIR spectra for to(LPEHM) hydrogel , the appearance of a new strong peak in the frequency range ($٣٣٥٠\text{ cm}^{-١}$) for to primary substitute amide , also disappearance moderate two peaks in the

frequency range ($3400, 3000$) cm^{-1} for unsubstitute amide and disappearance broad peak in the frequency range ($3400 - 3600$) cm^{-1} for (OH^-) group , this indicate the formation hydrogel polymer cross linking .

Fig.(2-13) show the FTIR spectra for to(LPEGa) hydrogel , the appearance of a new strong peak in the frequency range (3300 cm^{-1}) for to primary substitute amide, also disappearance moderate two peaks in the frequency range ($3400, 3000$) cm^{-1} for unsubstitute amide this indicate the formation hydrogel polymer cross linking .

Fig.(2-14) show the FTIR spectra for to(LPEC_v) polymer , the appearance of a new strong peak in the frequency range (1600 cm^{-1}) due to ($\text{C} = \text{N}$) bond , also disappearance moderate two peaks in the frequency range ($3400, 3000$) cm^{-1} for unsubstitute amide this indicate the formation hydrogel polymer cross linking .

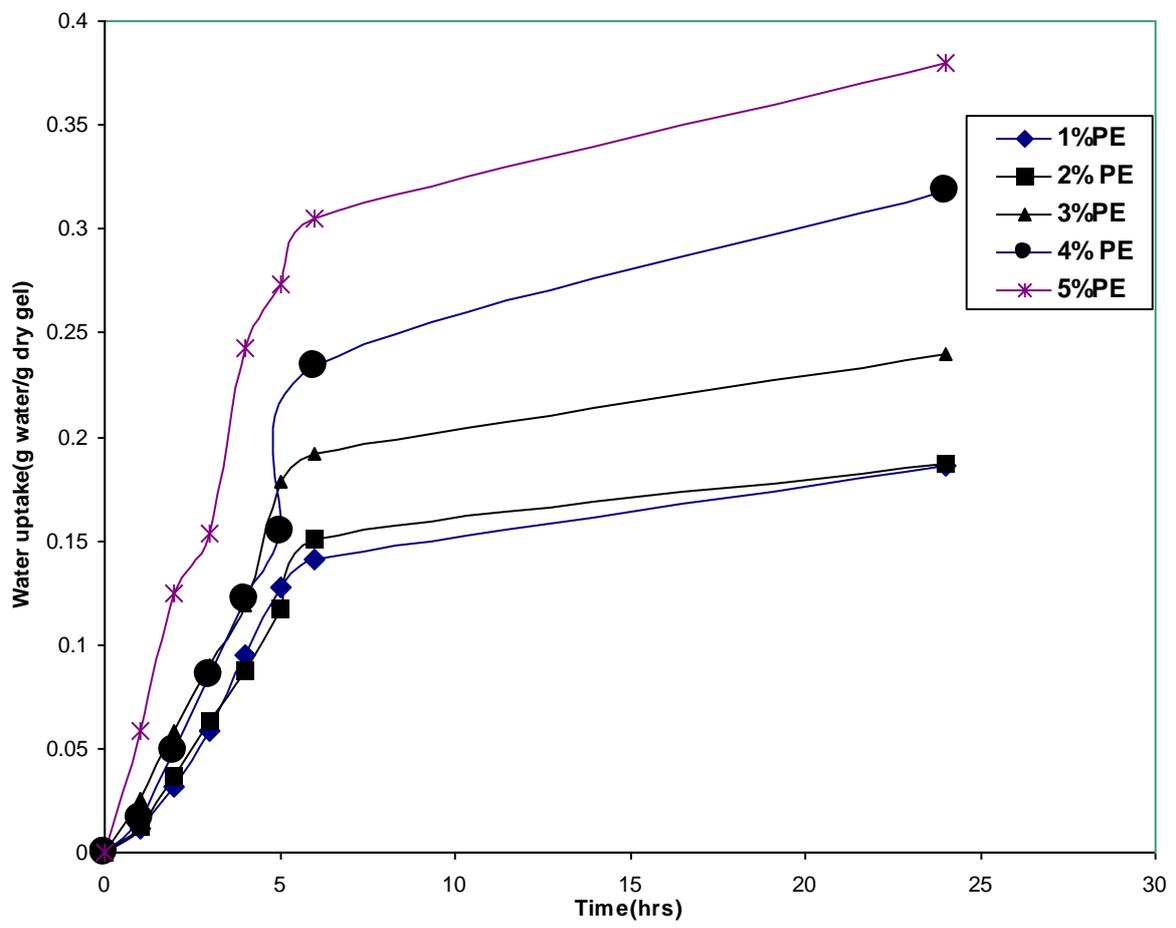


Fig.(3-1-1): Effect of hexamine (%) on the Water uptake (g water / g dry gel) of (LDPE with different ratio of PE) for [LPEHM] hydro gel .

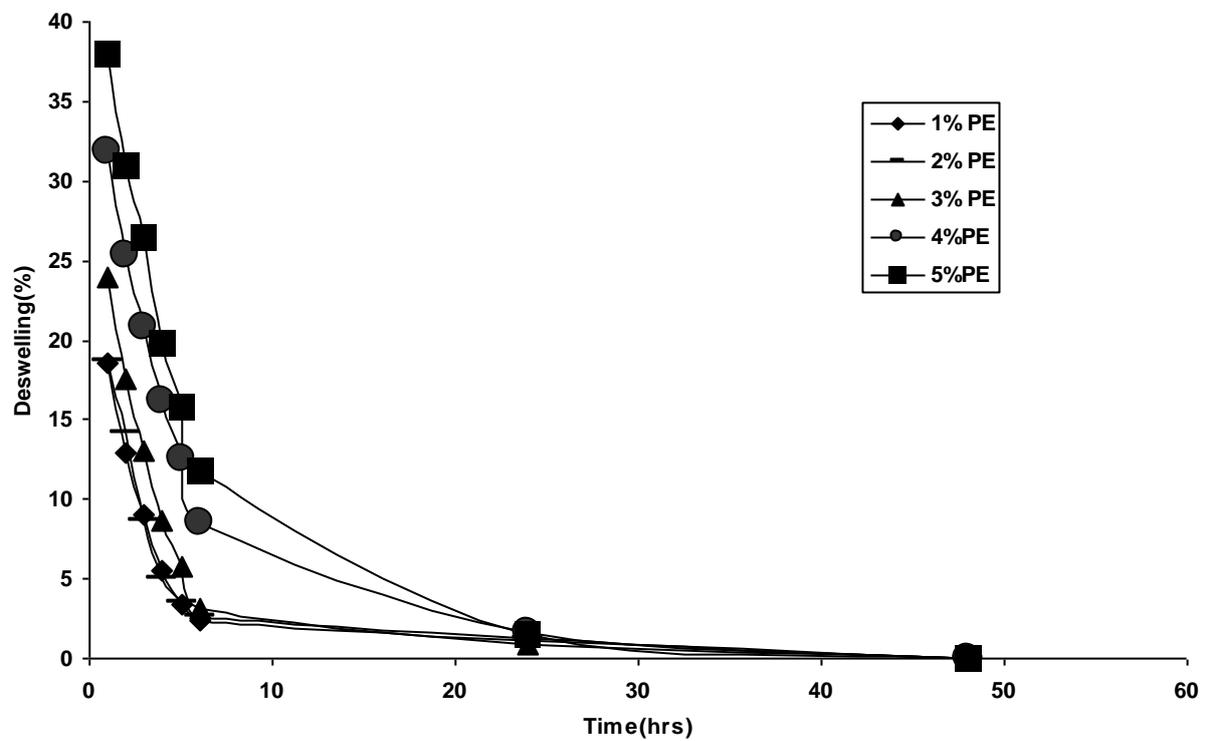


Fig.(3-10): Effect of hexamine (0%) on the Deswelling (%) of (LDPE with different ratio of PE) for [LPEHM] hydro gel .

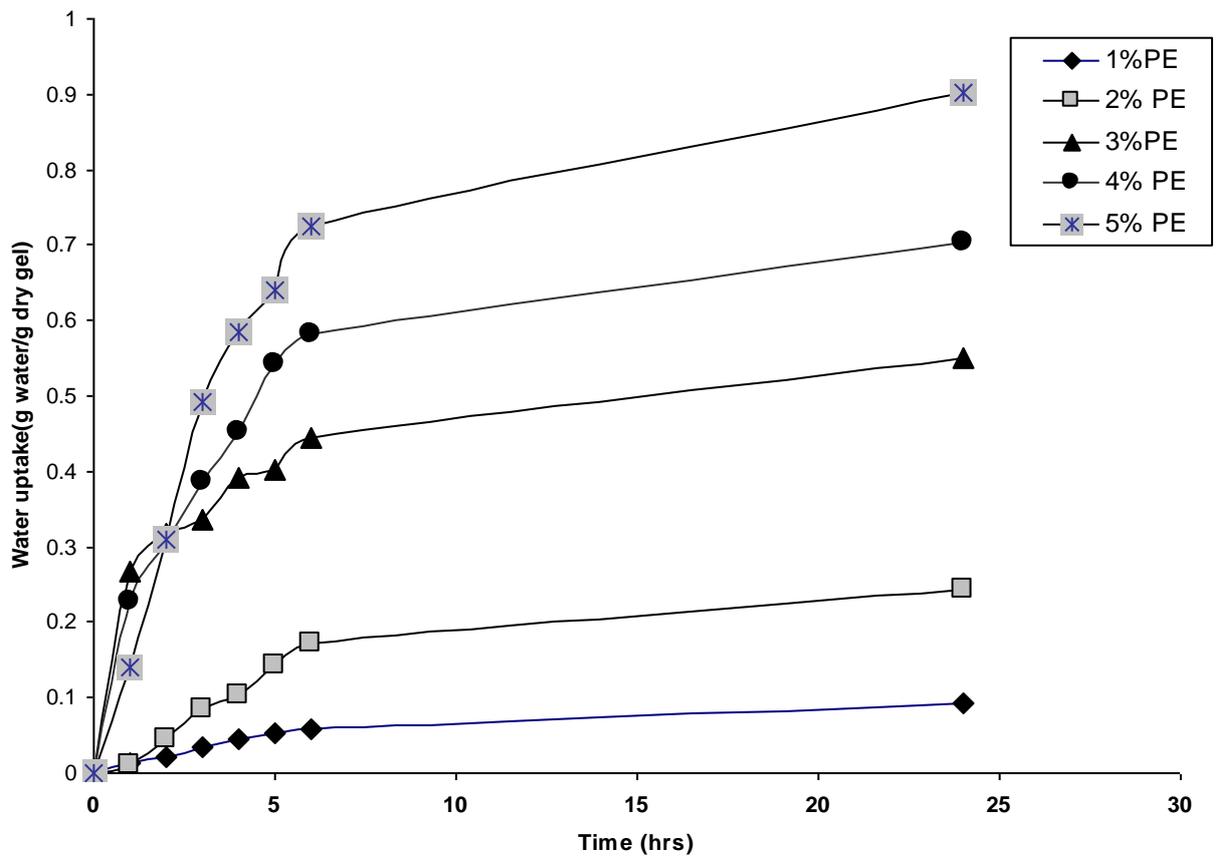


Fig.(3-10): Effect of Gluteraldehyde (2%) on the Water uptake (g water / g dry gel) of (LDPE with different ratio of PE) for[LPEGa] hydro gel .

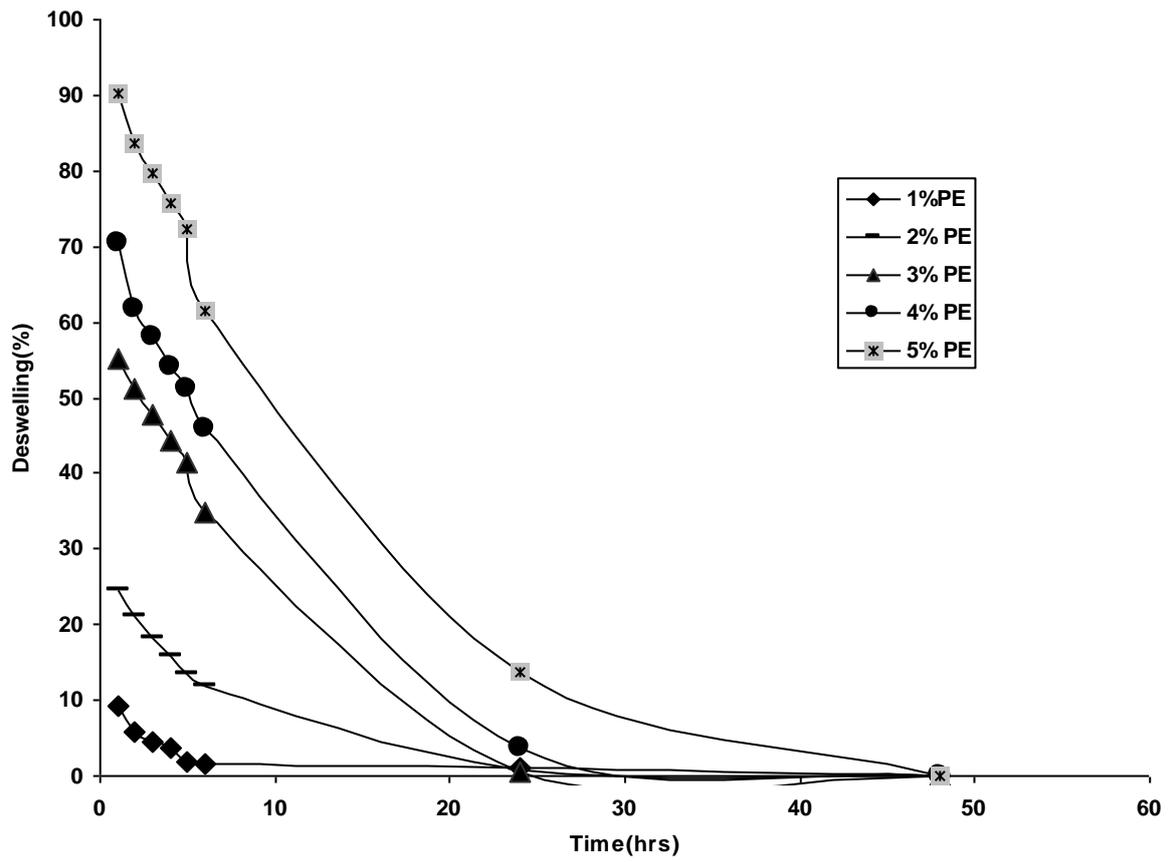


Fig. (3-1-4): Effect of Gluteraldehyde (%) on the Deswelling (%) of (LDPE with different ratio of PE) for [LPEGa] hydro gel .

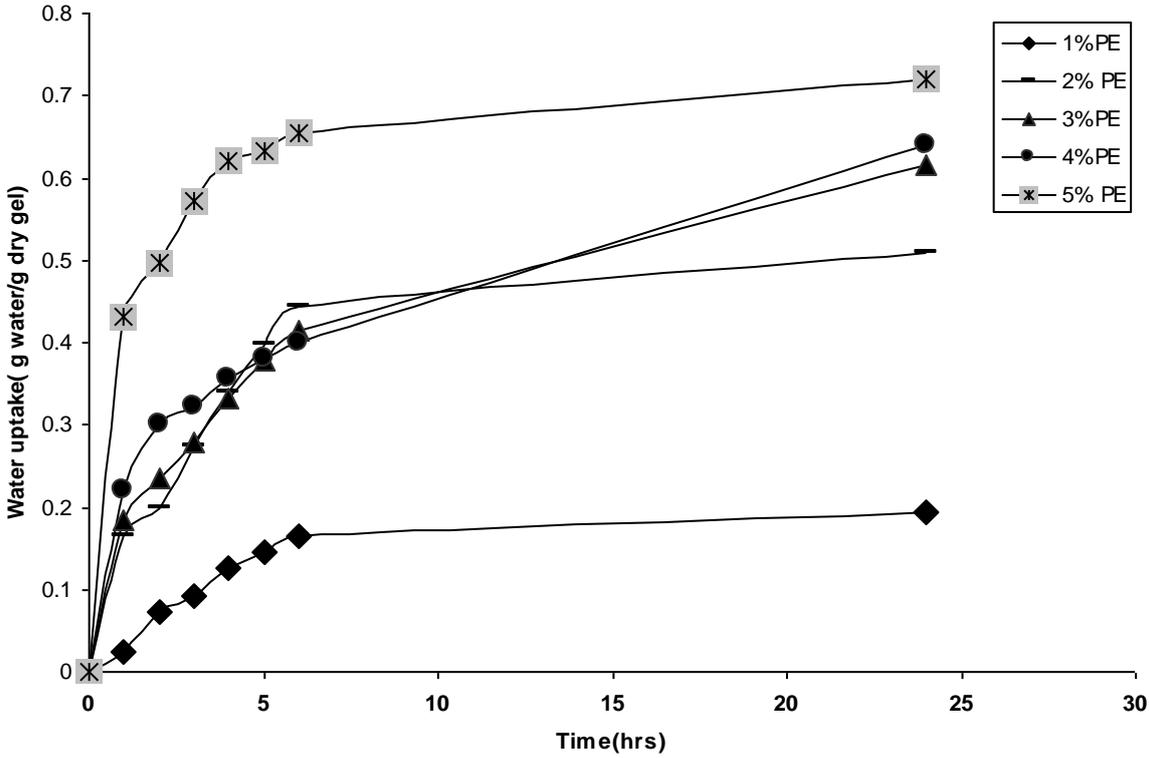


Fig.(3-10): Effect of C_{TV} (%) on the Water uptake (g water / g dry gel) of (LDPE with different ratio of PE) for [LPEC_{TV}] hydro gel .

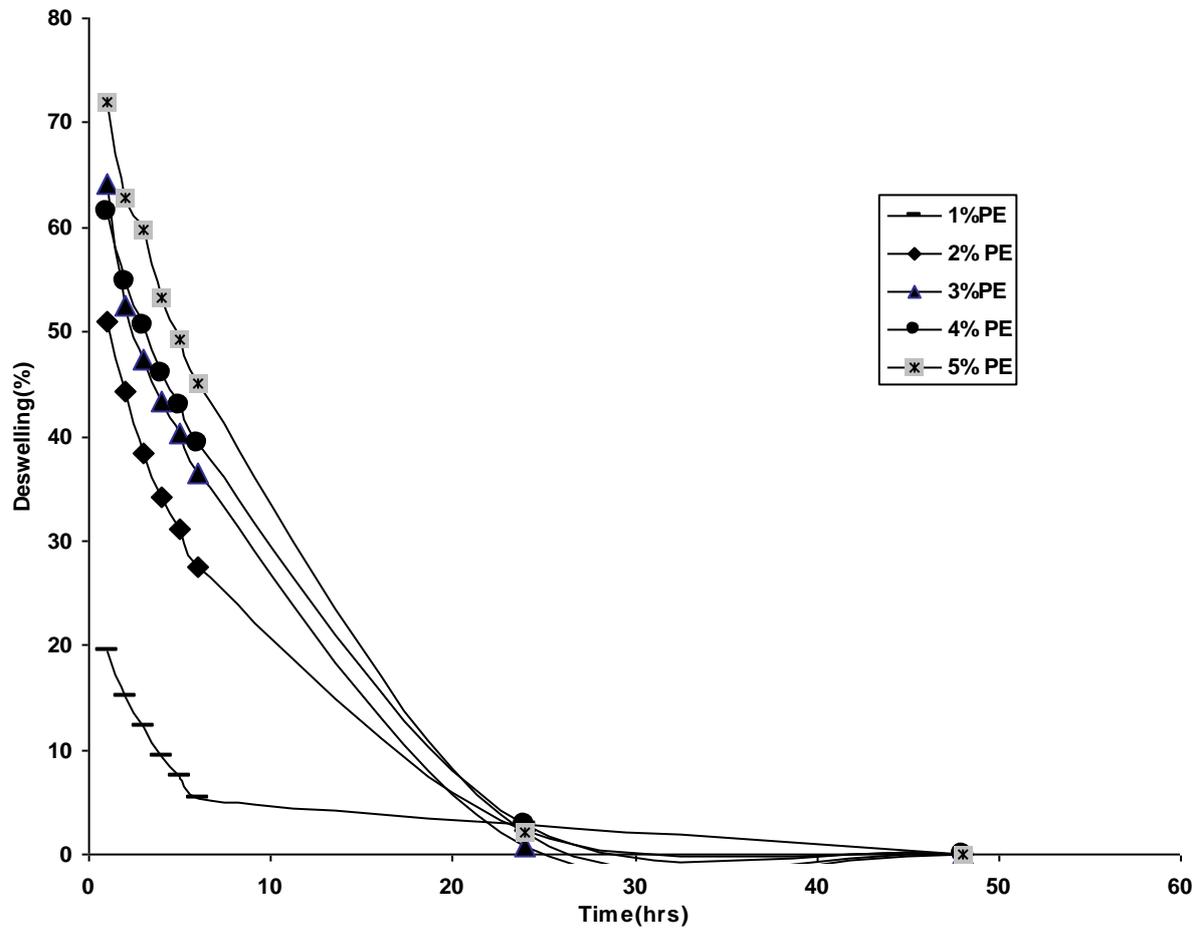


Fig.(3-10): Effect of C_{TV} (%) on the Deswelling (%) of (LDPE with different ratio of PE) for [LPEC_{TV}] hydro gel .

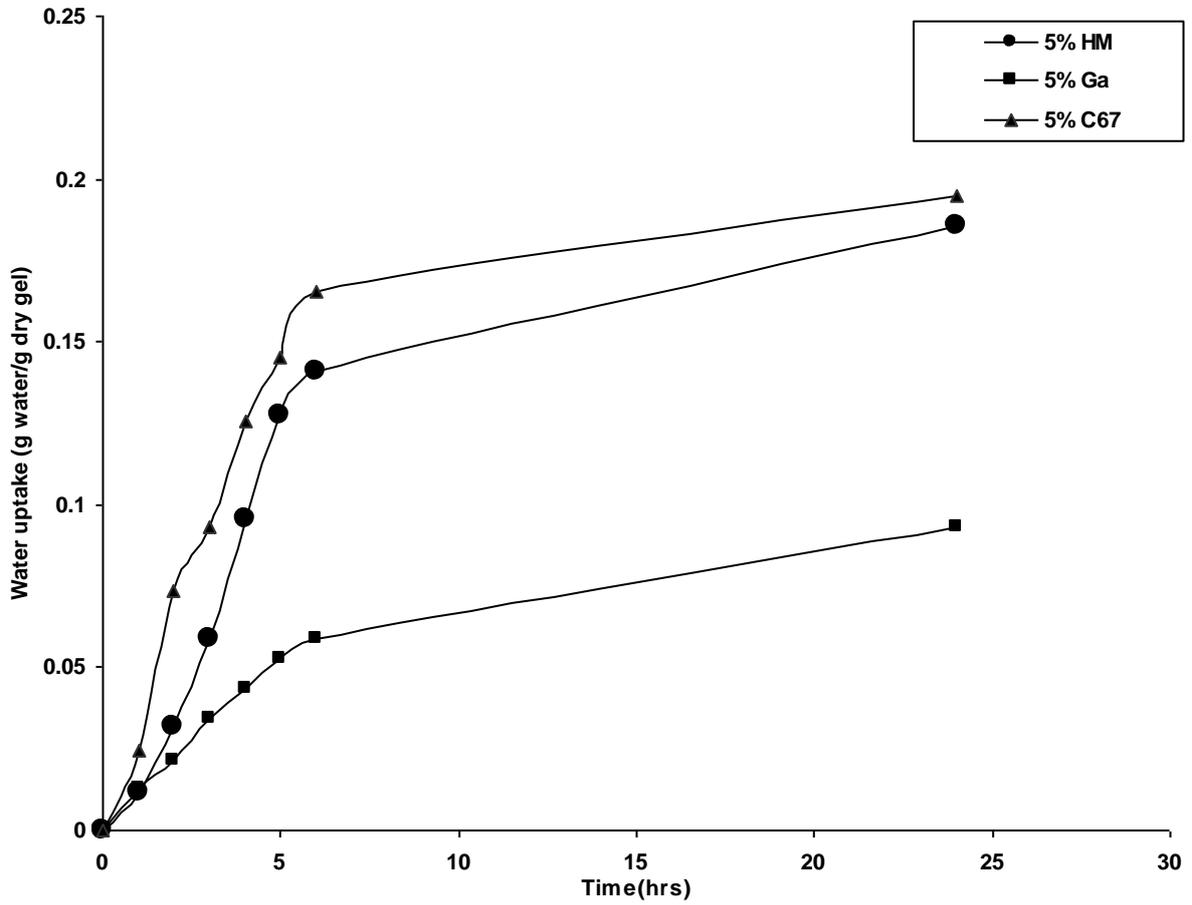


Fig.(3-10): Effect of HM , Ga , C₆₇ (%) on the Water uptake (g water / g dry gel) of (LDPE with 1% of PE) for [LPEHM , LPEGa , LPEC₆₇] hydro gels .

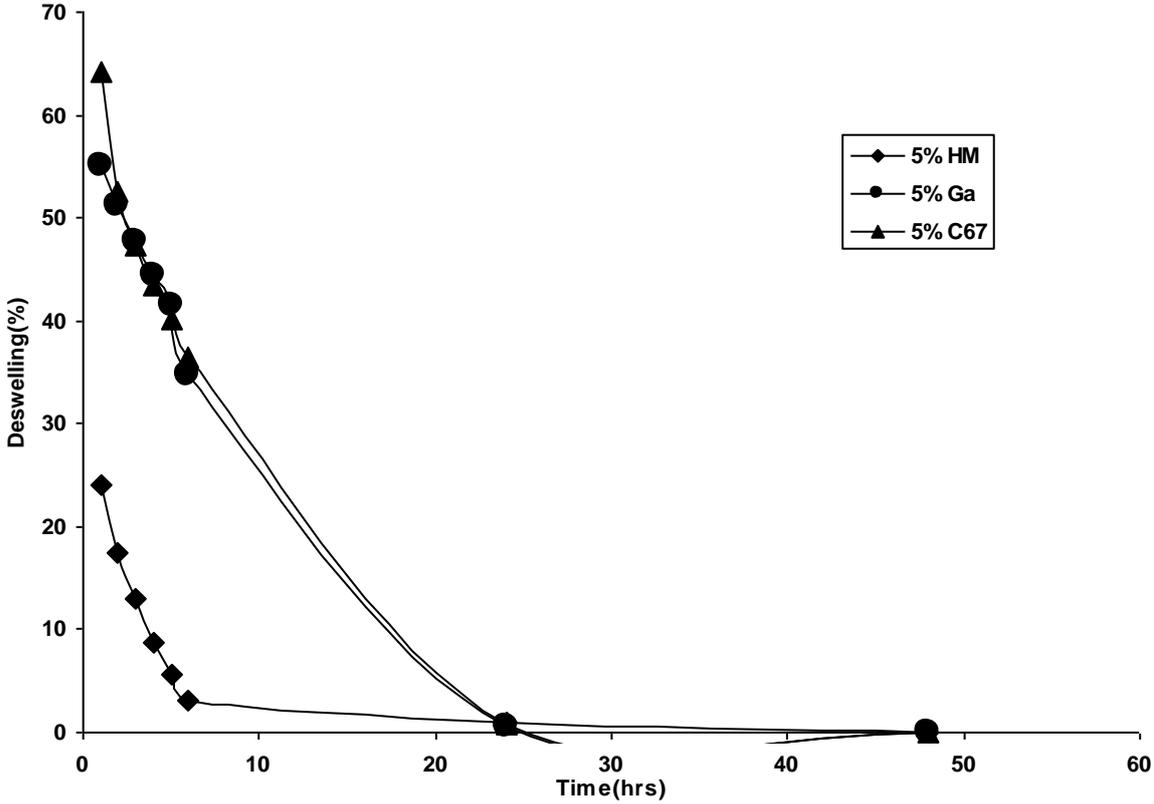


Fig.(3-10): Effect of HM , Ga , C₆₇ (%) on the Deswelling (%) of (LDPE with 1% of PE) for [LPEHM , LPEGa , LPEC₆₇] hydro gels .

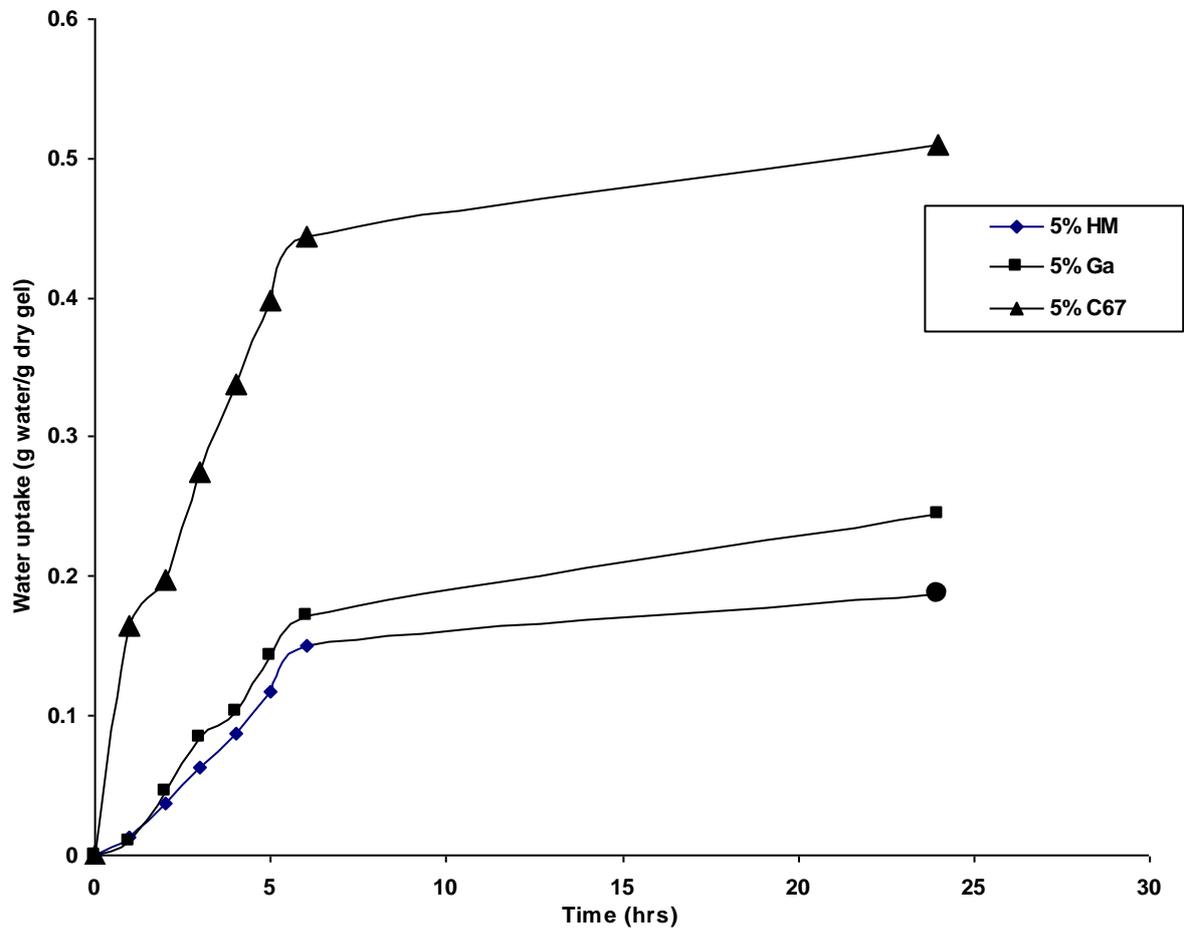


Fig.(3-109): Effect of HM , Ga , C₁₇ (%) on the Water uptake (g water / g dry gel) of (LDPE with 2% of PE) for [LPEHM , LPEGa , LPEC₁₇] hydro gels .

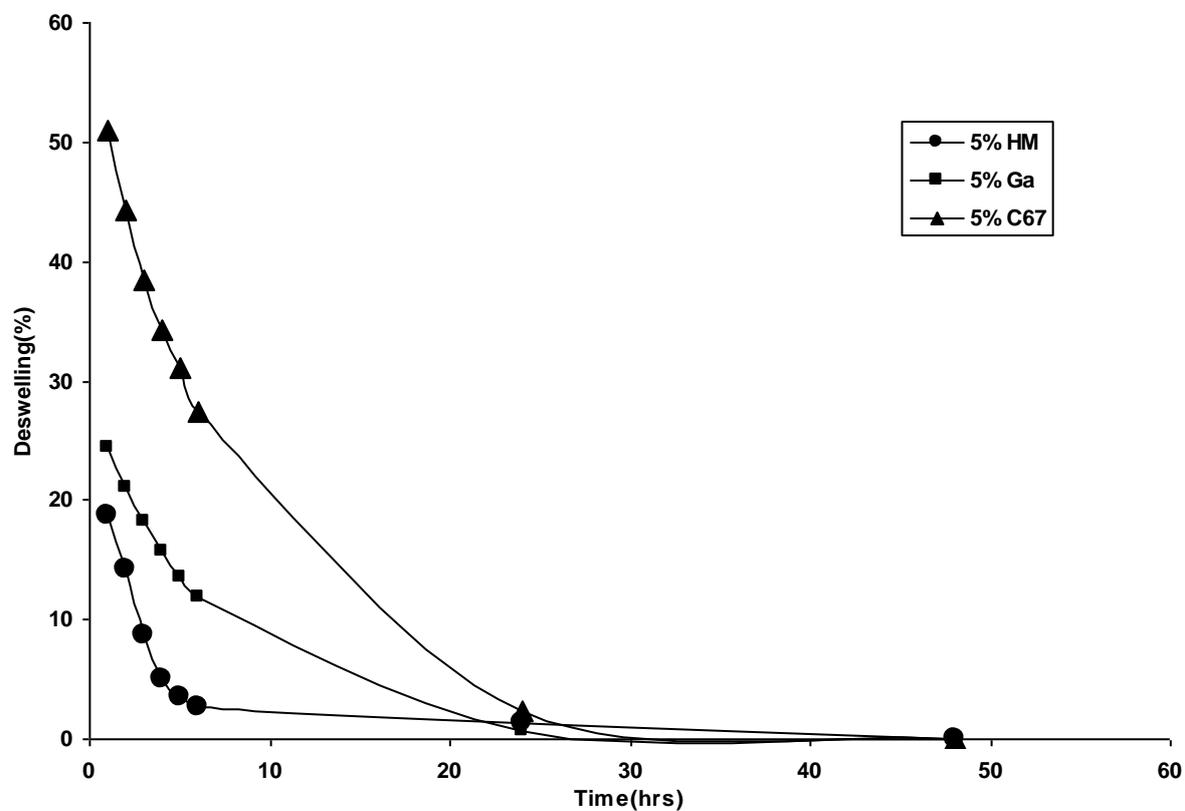


Fig.(3-110): Effect of HM , Ga , C₁₇ (%) on the Deswelling (%) of (LDPE with 2% of PE) for [LPEHM , LPEGa , LPEC₁₇] hydro gels .

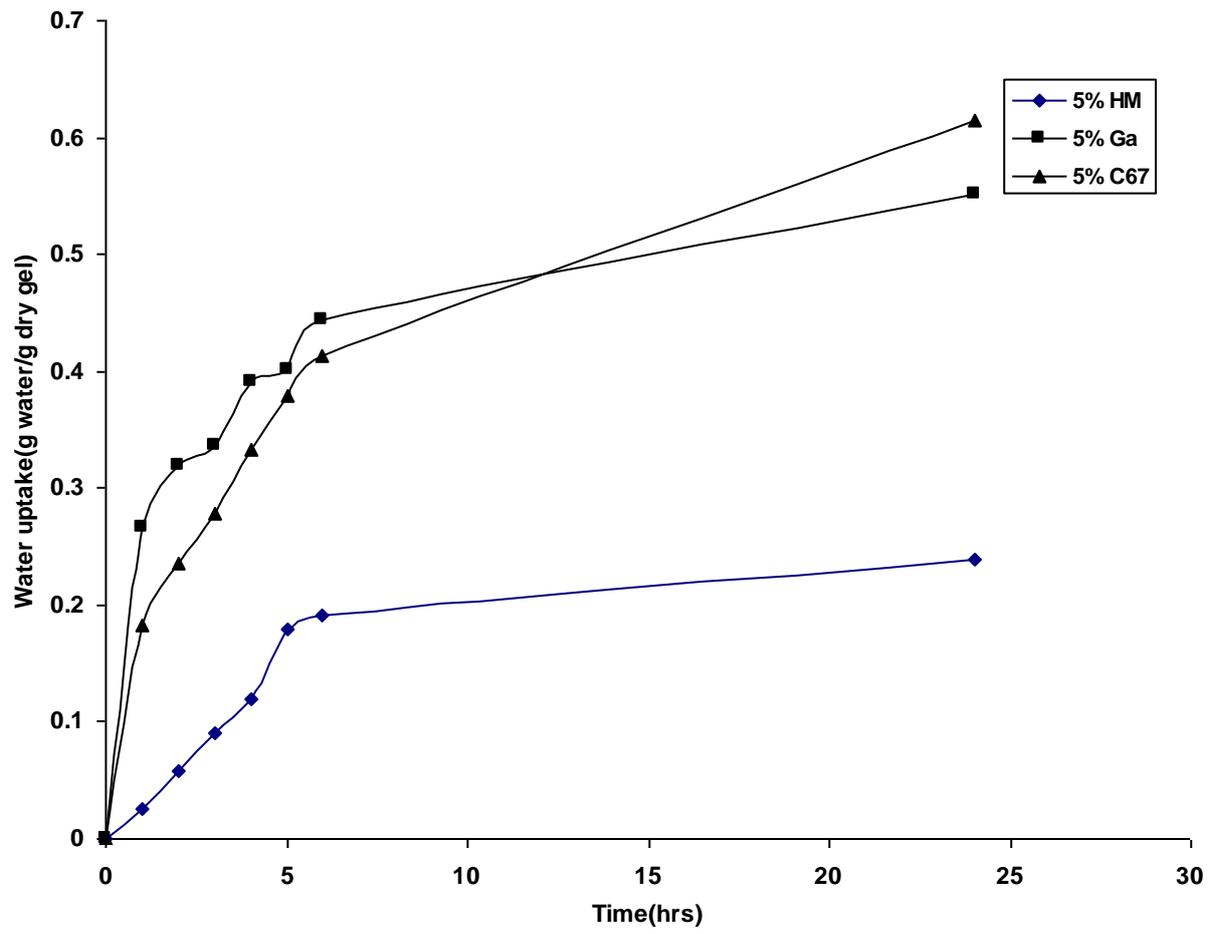


Fig.(3-111): Effect of HM , Ga , C_{7v} (%) on the Water uptake (g water / g dry gel) of (LDPE with 3% of PE) for [LPEHM , LPEGa , LPEC_{7v}] hydro gels .

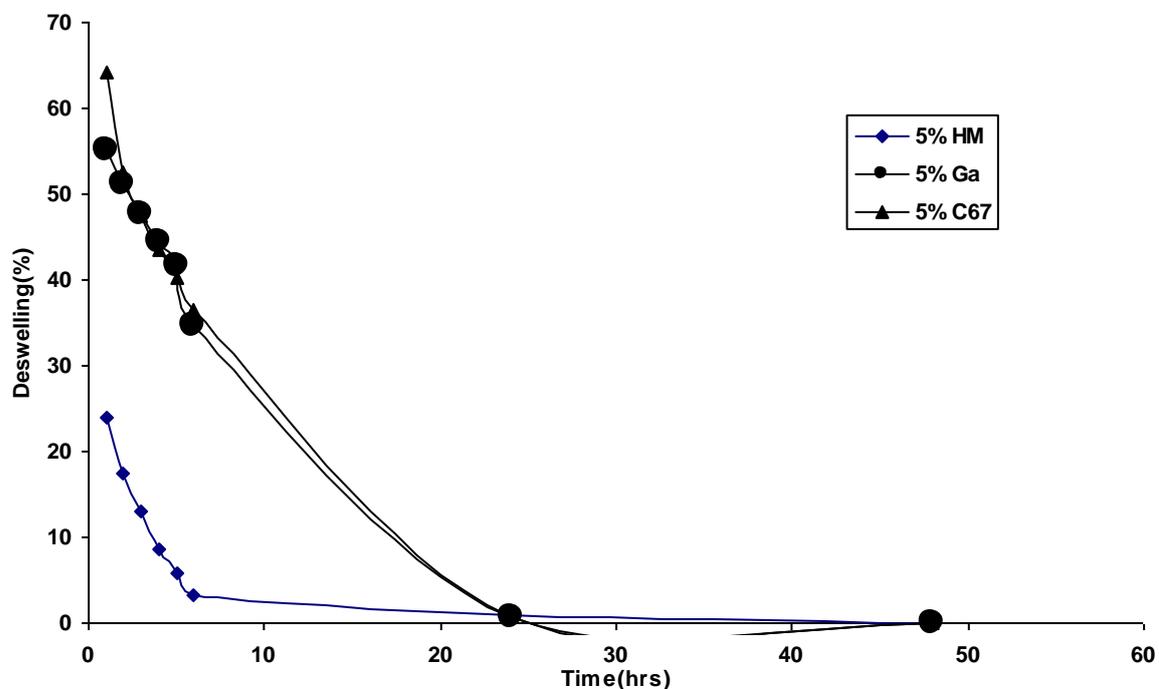


Fig.(3-112): Effect of HM , Ga , C_{7v} (%) on the Deswelling (%) of (LDPE with 3% of PE) for [LPEHM , LPEGa , LPEC_{7v}] hydro gels .

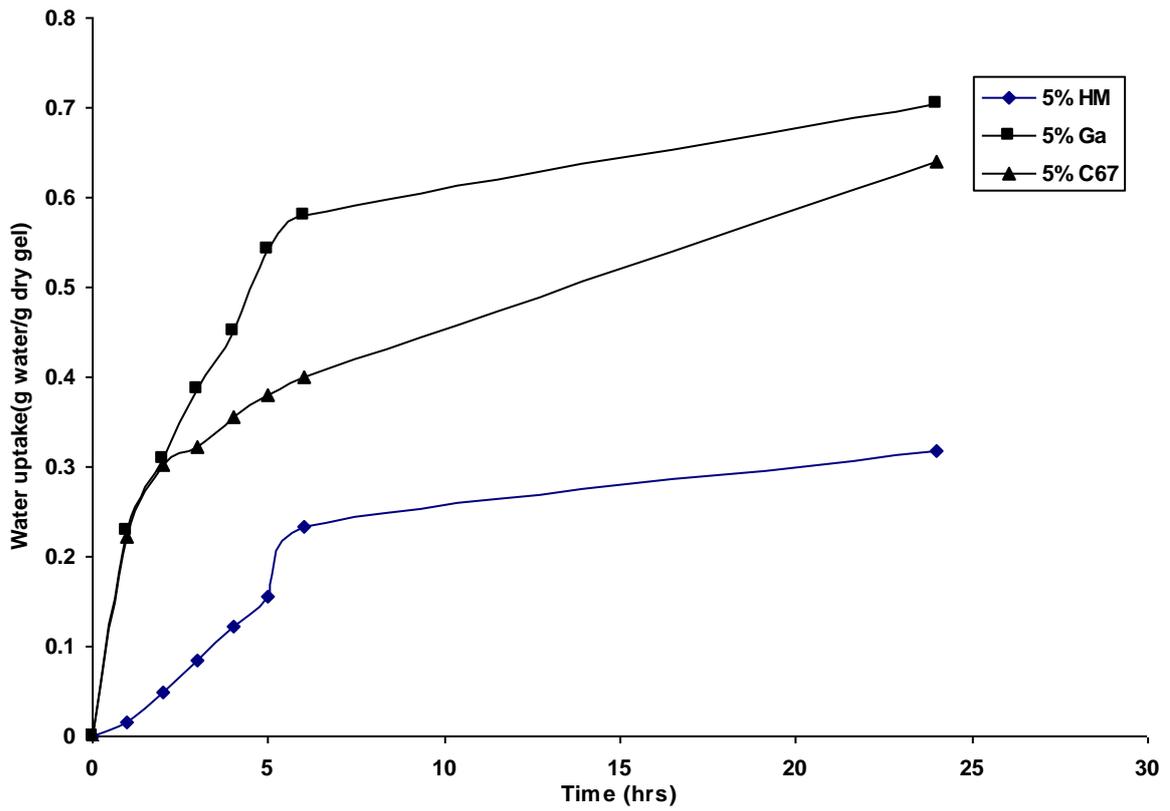


Fig.(1-11): Effect of HM , Ga , C₆₇ (%) on the Water uptake (g water / g dry gel) of (LDPE with 4% of PE) for [LPEHM , LPEGa , LPEC₆₇] hydro gels .



Fig.(3-11): Effect of HM , Ga , C₁₇ (%) on the Deswelling (%) of (LDPE with 4% of PE) for [LPEHM , LPEGa , LPEC₁₇] hydro gels .

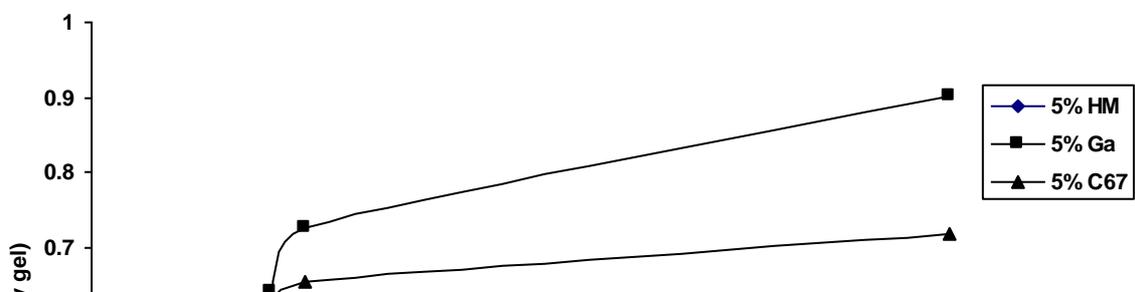


Fig.(3-11): Effect of HM , Ga , C₁₇ (%) on the Water uptake (g water / g dry gel) of (LDPE with 5% of PE) for [LPEHM , LPEGa , LPEC₁₇] hydro gels .



Fig.(۳-۱۱۶): Effect of HM , Ga , C_{۱۷} (°%) on the Deswelling (%) of (LDPE with ۰% of PE) for [LPEHM , LPEGa , LPEC_{۱۷}] hydro gels .

Conclusion

The program of this Ph.D study titled ; Synthesis of new Polymers, study of Electrical properties , Mechanical properties and study of Swelling and Deswelling ratio for new Hydro gels properties . Pointed out the basic important conclusions :

١- The Electrical Conductivity was increased when PVC composites filled Graphite than those filled Carbon black , due to the high Conductivity of Graphite .

٢- The increase in DOP concentration leads to increase the Conductivity increased .

٣- The increase in filler (C) or (G) the Activation energy was increased .

٤- The increase in temperature the resistivity was reduce , and the Conductivity is increased .

٥- Good mechanical properties was obtained when using new method in comprising the Sandwich method .

٦- An increased in tensile strength of prepared Polymers was noticed using

(C , G , PAM) as a fillers and (HM , Ga , C_{1V}) as a cross linking agents .

Y- A decrease in impact strength and in elongation with an increase in conc. of filler while increase in the hardness was noticed .

Λ- The polymer [LDPE and PAM] and the polymer[LDPE and PE] with (HM , Ga , C_{1V}) as a cross linking agents an optimum cross link density which leads to large swelling ratio were obtained .

Suggestions for future work

According to the obtained result suggest :-

- ١- The study other properties of Electrical Conductivity for polymers prepared , also the study of Conductivity for to other new polymers .
- ٢- In Electrical Conductivity for polymers using other fillers and other cross linking agents to the LDPE , HDPE polymers , also study using same fillers for to other polymers .
- ٣- Study Mechanical properties using (PAM) as a filler with other polymers .
- ٤- The study of other factors as a function for to hydro gels prepared in this study example (pH) .
- ٥- Different metals can be plated on the prepared polymer after enhancing the Electrical Conductivity for polymer .
- ٦- To used electrolysis to coat the Conductive polymer with certain metals

which would be more homogeneous and adherent .