Republic of Iraq
Ministry of Higher Education
And Scientific Research
University of Baghdad
College of Education for Pure Science / Ibn Al-Haitham
Department of Physics

Study the Effect of Heat Treatment on the Structural and Mechanical Properties for poly (tetrafluoroethylene)

A thesis

Submitted to the Counsil collage of Education for Pure Science / Ibn Al-Haitham - Baghdad University in Partial Fulfillment of The Requirements for the Degree of Master of Science in Physics

By

Rand Basim Lutfi Al Karkhy

BSc. in Physics / 2011

Supervised by:

Dr. May A.Mohamed Najeeb

1437 A.H **2015 A.D**

بِسْمِ اللهِ الرَّحْمنِ الرَّحِيمِ

" وَيَسْأَلُونَكَ عَنِ الرُّوحِ قُلِ الرُّوحُ مِنْ
أَمْرِ رَبِّي
وَمَا أُوتِيتُم مِنَ الْعِلْمِ إِلَّا قَلِيلًا "

صَدَقَ اللهُ الْعَظِيْم

سورة الإسراء الايه (85)

Acknowledgements

Thanks God for inspiring me with strength, willingness and patience to establish this work.

I am so grateful to everybody who has given me the support I needed to complete this work. My deep appreciation is extended to my supervisor Dr. May A. Mohammed Najeeb for her keen involvement and competent guidance in every phase of this work.

I would also like to express my gratitude and thanks to Deanship of college, and all Physics Department in "College of Education for Pure Science/Ibn Al Haitham" for all facilities they have offered.

Finally, I must not forget to express my deep gratitude to my family who have stood by my side in every possible way and my thanks to all my friends.

الأهداء

إلى من رضا الله من رضاهما
إلى من ترافقني دعواتهما
الى من فرشوا ايام عمرهما طريقا لأيصالي ..
الى من سهروا فصبروا طلبا لامالي ..
الى من اضاؤا لي عمرهما لتنير لي كل الأزمان ..
الى من طوقاني بالحب والحنان ليمحوا كلمة الحرمان ..
الى من لولاهما لما كنت هذا الانسان ..
الى قدوتي ومثلي الاعلى في حياتي ..
أمي و أبي
الى من منحوني الأمل وسراجي الذي ينير لي الطريق ... اخواتي (رشا - سجى)
إلى من أشد به أزري أخي الحبيب ... (محمد)
الى من علمني الأصرار والنجاح إلى من أحبني فأحببته ... (جدي رحمه الله)
الى امي الثانية التي تطوقني بالحنان (جدتي اطال الله في عمرها)
الى حبيباتي و رفيقات دربي (مريم – شهد)
إلى الذين أحببتهم وأحبوني صدقاً ... أصدقائي

والى كل قلب ينبض بالحب من أجلي
أهدي ثمره جهدي المتواضع

رند

I certify that this thesis entitled "Study the Effect of Heat Treatment on the Structural and Mechanical Properties for Polymer Poly (tetrafluoroethylene)" was prepared by **Rand Basim Lutfi** under my supervision at Physics Department, College of Education for Pure Science Ibn - Al- Haitham University of Baghdad as partial requirement for the degree of Master of Science in Physics.

Signature:
Name: Dr.May A.Mohammed Najeeb
Title: Lecturer
Address: Collage of Education for
Pure Science Ibn - Al - Haitham
University of Baghdad

Date: / 4/ 2016

Report of the Head of Physical Department

In view of the available recommendation, I forward this thesis for debate by the examination committee.

Signature:
Name: Dr. Kareem Ali Jasim
Title: Professor
Address: Collage of Education for
Pure Science Ibn-Al-Haitham
University of Baghdad

Date: / 4 / 2016

Committee Certification

We certify that we have read this thesis titled" **Study the Effect of Heat Treatment on the Structural and Mechanical Properties for polymer Poly (tetrafluoroethylene)** " submitted by **(Rand Basim Lutfi**) and as examining committee examined the student in its content and that in our opinion it is adequate with "very good" standard as thesis for the Degree of Master of Science in Physics.

Signature:
Name: Dr.Najiba A. Hassan
Title: Professor
Address: The University of Mustansiriyah
(Chairman)
Data: / / 2016

Signature:
Name: Dr. Suad H. Laibi
Title: Assist Professor
Address: University of Baghdad
(Member)
Data: / / 2016

Signature:
Name: Dr. Abbas K. Saadon
Title: Assist Professor
Address University of Baghdad
(Member)
Data: / / 2016

Signature:
Name: Dr.May A. Mohamed Najeeb
Title: Lecturer
Address: University of Baghdad
(Member - Supervisor)
Data: / / 2016

Approved by the Council of the College of education for pure Science Ibn- Al-Haitham University of Baghdad

Signature:
Name: Dr. Khalid F. Ali
Title: Asst. Prof.
Address: The dean of Education Collage For Pure Science/Ibn al-Haitham
Date: / / 2016

Abstract:

In this study two modifications of pure polytetrafluoroethylene (PTFE) $[C_2F_4]_n$

It seems that the product company of china is better than the product company of UAE in degree of crystallinity and mechanical properties for this polymer.

Subject		Pages

Chapter One
Introduction & Literature review

1-1	Introduction	1
1-2	Literature Review	4
1-3	The Aim of Study	12

Chapter Two
Theoretical Part

2-1	General Concepts	13
2-2	Classification of Polymers	13
2-2-1	Classification Based on Source	13
2-2-2	Classification Based on Structure of Polymers	14
2-2-3	Classification Based on Mode of Polymerization	15
2-2-4	Classification Based on Thermal Behavior	15
2-3	Fluorocarbon	16
2-4	Principle of Powder Diffraction	18
2-5	Polymers and Plastics	19
2-6	Crystallinity	19
2-6-1	By X-Ray Diffraction	20
2-6-2	By Differential Scanning Calorimetry	23
2-7	Mechanical Properties	25
2-7-1	Tensile Test	25

Chapter Three
Experimental Part

3-1	Sample Used	29
3-2	Thermal Treatment	30
3-3	Powder Diffractometer	30
3-4	Differential Scanning Calorimetry (DSC)	31
3-5	Mechanical Property Test	32

Chapter Four
Results & Discussion

4-1	Crystallinity	34
4-1-1	The Degree of Crystallinity from X-Ray Diffraction (XRD)	34
4-1-2	The Degree of Crystallinity from Differential Scanning Calorimetry (DSC)	44
4-2	Shrinkage	52
4-3	Mechanical Properties	53
4-3-1	Tensile Test	53

Chapter Five
Conclusion & Suggestions for Future Works

5-1	Conclusion	62
5-2	Suggestions for Future Work	63
	References	64

List of abbreviations and Latin symbols

Abbreviation/ Symbol	*Meaning*
PTFE	Poly(tetrafluoroethylene)
TFE	(tetrafluoroethylene)
I_{cal}	The intensity calculated
X_t	Angle 2Ө
A_t	Peak height
Pt	Angular location of top peak
n	Number of height peaks calculated
I_t (2Ө)	Totally scattering for separated peaks in the spectrum
I_{nor} (2Ө)	Totally scattering for spectrum
B	Number of separated peaks in spectrum
(IC	Intensity of crystalline region
I_a	Intensity of amorphous region.
X_C	The crystallinity of polymer
ΔH	The quantity of Enthalpy melting of the sample
$^{\circ}\Delta H$	The quantity of Enthalpy melting of the sample totally crystalline.
ΔL	The change in length
Å	Angstrom
Pa	Pascal's
L	Length
W	Width

Y	Young modulus
σ_B	stress at breakdown
σ_y	stress at yield point
ε_B	strain at breakdown
ε_y	strain at yield point

1-1 *Introduction*

The industrial and scientific importance of the science of polymers has increased dramatically in the late last century, global statistics have estimated that more than 20% of engineers and 40% of scientists are working in the fields of plastic industries and technologies [1].

Today engineers and designers easily turn to plastics because they possess a number of features which are not available in any other materials.

Plastics characterizes by resistance to corrosion, lightness, colour fastness, transparency, resilience, ease of processing, etc. [2].

The Polymer materials are large molecules consisting of repeated chemical units (`mers' at least five) joined together as a beaded string. Polymers typically contain many more than five monomers, and some may contain hundreds or thousands of monomers in each series [3].

They own private advantages (ceramic and metal) including easy production ,light weight, low density , cheap price, and high durability, as it does not corrode or rust , its electrical and thermal conductivity is low, so it is used as electrical and thermal insulators [4].

In this study, one of thermoplastic polymers was used; it is Polytetrafluoroethylene - (PTFE) $[C_2F_4]_n$.

Polytetrafluoroethylene is a linear branchless extremely crystalline polymer with a melting point of (327 °C) and related to the family of fluoro plastics.

PTFE had been chosen for a number of reasons which include; its availability from many manufacturers and its use as a common engineering material for small high performance parts. Although it had been studied thoroughly in the past, it had little attention in the open literature for the past (25) years. We have decided to restudy PTEF due to the lack of its mechanical data and its structural complexity. It is an exceptional material in many ways; it offers some beneficial properties over the widest temperature range in a better way than does any other polymer. It is resistant to almost all caustic and acidic materials and it is insoluble in all common solvents. PTFE has the highest resistivity of any material, low dielectric loss and a very high dielectric strength. The sliding friction coefficient between PTFE and many of engineering materials is very low and when sintered with wear reducing compounds, an industrially remarkable class of bearing materials is produced [5].

Application of PTFE:

In numerous applications, tetrafluoroethylene (TFE) is co-polymerized with other fluorinated monomers, such as hexafluoropropene and perfluoropropylvinyl either and ethane. Poly (tetrafluoroethylene) (PTFE) and its co-polymers are used in:

- Tubing and Hose.
- Cable insulation.
- Reactor and plant equipment linings, when reactants or products are highly corrosive to ordinary materials like steel.
- Semi-permeable membranes in chlor-alkali cells and fuel cells
- Components and bearings in mechanical devices like small electrical pumps and motors.
- Permeable membrane for shoes and clothing which allows water vapor to diffuse away from the skin but prevents liquid water from soaking in.
- Non-stick domestic utensils like frying pans.
- The Medical-catheter tubing.
- Solid lubricant.
- Powdered PTFE is used as an oxidizer in pyrotechnic compositions with powdered metals like magnesium and aluminum. When

ignited, these mixtures form carbonaceous grime and release large amounts of heat and the corresponding metal fluoride. They are used in infrared flares and as igniters for solid-fuel rocket propellants. PTFE and Aluminum are used in some thermobaric fuel compositions as well.

- By virtue of its structure, PTFE is composed into semi- finished products using compression machines and processes then with cutting/ machining devices [6].

1-2 Literature Review:

- **Bradley K. Smith et al**. In (1998) presented initial reliability studies and film properties for thin Teflon films applied to a unique test vehicle; the artificial Sandia-designed microengines. The results were microengines coated with the film showing an order of magnitude reduction in the friction coefficient and a factor of three improvements in their lifetime when compared with uncoated specimens. [7]

- The molecular conformations of polytetrafluoroethylene were studied by **E.S. Clark** in (1999) the crystalline framework of Teflon is unique in possessing some crystal shapes, it possesses a fundamental molecular motion within the crystal in temperatures lower than the melting point and shows the unique first order transition that occurs at about (19°C) changing the crystal structure from form II to form I (first and second order).electron diffraction data and X-ray from forms (II) and (IV) (phase diagram) are translated as Spiral structures. [8]

- **Duncan M. Price and Mark Jarratt** studied the thermal conductivity of Teflon in (2001) by utilizing (DSC) and an instrumented thermal conductivity device. The previous method has been used to show the effect of integrating fillers into a PTFE glass fiber fabric utilized for the conveyor belts in food processing. The result of crystallinity on thermal conductivity has been surveyed; they compared different methods of crystallinity determination. Heat transport through the composites was improved by integrating Aluminum flakes. [9]

- In (2002) **Yong Qiu et al**. studied PTFE which was used as insulating layer to modulate the efficiency of organic light emitting diodes. PTFE film assisted to effectively hinder indium diffusion from the ITO electrode and to boost the hole tunneling injection. In comparison with tools without PTFE, the turn on voltage was lowered by (1.5 V) because of the introduction of PTFE buffer and the optimized tools manifested a luminous efficiency double than that of the tools without Teflon layer and the device lifetime was confirmed to be staggeringly raised. [10]

- In (2004) the properties of PTFE under the effect of compression were studied by **P.J.Rae and D.M.Dattelbaum**. Samples of Teflon were tested under compression at temperatures between (-198 and 200 °C) and strain-rates between (10^{-4}) and ($1s^{-1}$).The mechanical properties have been discovered to be strongly influenced by temperature and strain-rate. [5]

- Also in the same year **Taketo Kitamura et al.** studied the progression of membrane characteristics and morphological changes caused by heat treatment which were researched for PTFE porous membranes prepared from fine powder by extrusion, rolling and stretching. Heat treatment had altered the properties of the membrane in a significant way. The partial melting of polytetrafluoroethylene makes the shrinkage diminish and the mechanical strength increase. The reason behind that is the inhibition of making new fibril due folded ribbon loss such as crystalline structures that facilitate fibril structures to be withdrawn outside the main (PTFE) particle. The nodes union in the stretching orientation was the most significant change in the porous structure resulted by heat treatment which led to the formation of porous membrane with larger spatial periodicity. Heat treatment of a degree higher than the melting temperature of (PTFE) was the most functional [11].

- In (2005) **L. Ylianttila et al**. explained that polytetrafluoroethylene is the most widely utilized diffuser material in ultraviolet irradiance measurements. PTFE temperature sensitivities diffusers were calculated over a wide temperature range. Because the crystal structure of PTFE changes at (19 °C), the transmittance will also change; temperature sensitivity dramatically lowers the precision of the measurements mostly if the temperature of the diffusers is not steady [12].
- During the same year **N.L. McCook et al**. studied a composite coating of PTFE. This coating has been produced by soaking an extended PTFE film with epoxy. The promoted tribological attitude of these composites was thought to be originating from the coatings ability to draw thin (PTFE) transfer films into the contact from the nodes of (PTFE) that function as containers. Nano indentation mapping of the coatings that accompanying the scanning electron microscopy surveillance of the worn and unworn coatings in addition to the transfer films support this hypothesis. [13].

- Also in (2005) the ratcheting behavior under compression and the loading rate dependence of stress–strain reaction for poly (tetrafluoroethylene) had been studied by **Xu Chen et al.** It is clarified that poly (tetrafluoroethylene) depends on rate but it will be insensitive to loading rate if the rate exceeds (40 N/s) ratcheting strain rises when loading rate losses [14].

- The micro structural and mechanical properties of high density PTFE composites were studied by **Jing Cai et al**. in (2007) PTFE matrix, tungsten particles (W) and aluminum (Al) were examined. Three specimen types having different particle sizes and porosities of (W) with similar weight ratios between (PTFE) and (Al) were manufactured by cold isostatic pressing. The outcomes proved that the porous (PTFE) composite specimens that contain fine tungsten particles have higher dynamic fracture stresses than the higher density (PTFE/AIAV) specimens that contain coarse tungsten particles. ESEM micrographs implied that deformation occurred essentially in the PTFE matrix however metal particles remain unreformed. [15].

- In (2009) specimens of Teflon were studied by the use of x-ray diffraction by **Yu.Lebedev et al**. At first a quantitative x-ray powder diffraction analysis of three components of the polymer has been carried out. All specimens of Teflon were figured out to be three-phased contain two amorphous phases and one crystalline phase. One of the amorphous phases is formed of low molecular weight output, the structure of this phase was at first confirmed by computer simulation and XRD methods [16].
- In the same year Nisreen Sabah Ali studied Osmotic membrane distillation; her experiments were performed with real system (pure water) in a flat sheet membrane module type Polytetrafluoroethylene (PTFE) macroporous layer supported by a polypropylene (PP) net with 0.00275 m^2 total surface area of the membrane was used.

Experimental results indicated that transmembrane flux increases with the increase of the osmotic agent concentration both of calcium chloride $CaCl_2$ and sodium chloride NaCl and decreases with the increase of time (0-3) hours at constant concentration then the efficient flux point at initial few minutes started experiment due to membrane fouling [17].

- **M. Yari et al**. also in (2009) studied the influences of varied solid substrates including; alumina ,carbon nanofibers (CNFs), poly vinyl pyrolidone (PVP) ,activated carbon, and silica which were matched for high pressure synthesis of PTFE $(CF_2)_n$ nanoparticles by means of the reduction of thermally synthesized tetrafluoroethylene (TFE, C_2F_4) as monomer. Different solid materials were found to have varied capacities to form (PTFE) nanoparticles depending on their shape, size and morphology. The sizes and amounts of synthesized (PTFE) nanoparticles de facto depend highly on the nature of the solid surface substrate [18].

- In (2010) **KHARDE et al.** studied the tribological characters of glass fiber (GF) filled polymer composites keeping in mind three velocities. The test has been performed for three materials (PTFE + 35% GF), (PTFE + 25% GF), (PTFE + 15% GF), and in oil (wet) and by using additive like graphite (5% wt) in oil, it has been detected that wet conditions and load have a major influence on specific wear rate of the materials and friction coefficient; whereas sliding velocity plays a trivial role in the wear mechanism of the material. It is inferred that specific wear rate in wet conditions by using additives in lubricating oil with 5% by (wt) has dropped and the specific wear rate has decreased by the sliding velocity and normal load [19].

- In the same year the recognition of PTFE by the use of sophisticated thermal analysis techniques was studied by **J. Blumm, et al**. Thermal description of a PTFE material was performed by the use of thermos-physical properties test techniques and various thermal analyses. The specific heat and transformation energetics have been measured using differential scanning calorimetry (DSC). The density changes and thermal expansion were set using pushrod dilatometry. The viscoelastic properties (loss modulus and storage) were experimented by using dynamic mechanical analysis. The thermal diffusivity was measured by utilizing laser flash technique. Combining thermal diffusivity data, density and specific heat allows to measure thermal conductivity of the polymer [20].

- In (2011) **Nunes et al**. work in tensile tests carried out in various strain rates by the use of standard samples. The strains are calculated by a non-contact video extensometer. This method is precise in particular due to the involvement of big deformations. The main aim is to estimate the stress-strain curve under various strain rates using simple mathematical equations to permit using them in engineering problems with the ability to describe complex non-linear mechanical behaviors. The constant materials that show in the sample equations can be simply distinguished by only three tests carried out at various constant strain rates. The outcomes of the test have shown a good harmony in comparison to the model predictions [21].

- In the same year **Rodrigo Canto et al**. performed thermal dilatometer analyses on samples made of filled or pure (PTFE) powders. The samples have been obtained by isostatic pressing or by uniaxial compaction up to various values of the residual void ratio. The large deformations that were recorded during different heating-cooling treatments rely mainly on the level and mode of compaction, as well as on the presence or the absence of fillers. Besides, these deformations are strongly anisotropic when the specimens are obtained by uniaxial compaction. It has been shown that this macroscopic deformation observed during sintering results from the combination of various mechanisms viz. thermal expansion, void closure, recovery, crystalline to amorphous phase change and vice versa, that were identified by varying the heat treatments [22].

- In the same year also **Cihat Gül et al**. studied a modern design (Polytetrafluoroethylene) radial lip seal was experimentally investigated. The aim of this work is to compare new design seal considering the commercial elastomer lip seal and their seal life frictional torque. For this aim, a test system has been improved in which a cylinder block is placed on four load cells to monitor the frictional torque generated between counter face and seal. At the end of many systematic experiments, the properties of new design PTFE seal have been obtained [23].

- In (2013) **Atta et al**. studied the structural and thermal properties of polytetrafluoroethylene (PTFE) modified by argon and oxygen plasma. The effects of plasma treatment on physio-chemical properties of PTFE surface have been determined by different characterization techniques viz, X-ray diffraction technique (XRD), Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM).The Plasma beam irradiation induces chain separation in the polymer which led to a decrease in crystallinity, the forming of relative stability free radical and reduction in thermal stability of the polymer [24].

- **MinJoong Kim et al**. also in (2013) explained the influences of heat treatment time on electrode structure and electrochemical characteristic of poly (tetrafluoroethylene) bonded membrane electrode assemblies for polybenzimidazole based rise temperature proton interchange membrane fuel cell. Results showed as the heat treatment time increases, only the large pore (secondary pore) volume in the electrode decreases, resulting in increase in mass transport resistance and concentration over potential in the high-current-density region [25].
- In (2014) **Mihai Dumitraş** studied the particles of PTFE that are obtained by mechanical processing of the formed polymer (Teflon bar). In order to assess the effect of mechanical wear on polymer properties, their melting and crystallization behavior was investigated by DSC and DTA, and the results were compared to the ones obtained for the native polymer. An increase of the crystallinity degree and an accentuated decrease of the average molecular weight were found for the samples submitted to mechanical wear, as a result of mechanical degradation of the polymer [26].

1.3 The aim of research:

As a result of the importance that have appeared in previous years in the use of polymers in general, and plastic materials in particular and in various advanced industrial applications.

The purpose of the survey is to;

1- Study the effect of heat treatment on crystallinity for two types of (PTFE) origins.

2- Study the mechanical properties of (PTFE) at different temperatures.

2.1 General Concepts

“Polymer” is a term came from the Greek words poly and meros, which mean many and parts respectively. Sometimes the word ‘‘macromolecule,’’ is preferred to be used by some scientists [27].

The binding of numerous quite smaller molecules is the way to build up polymers. “Monomers” is the term used to name the tiny molecules which join together to compose the polymer, and the term polymerization is used to name the reaction by which they combine [28].

2-2 Classification of Polymers: [29-32].

Polymers can be classified according to several considerations; the followings are some of the popular classification methods.

(2-2-1) Classification Based on Source:

There are three subcategories under this sort of classification.

a- Natural polymers:

This type exists in animals and plants. Like starch, proteins, some resins, rubber and cellulose

b- Semi synthetic polymers:

Those are cellulose derivatives, their paradigms include; rayon (cellulose acetate) and cellulose nitrate, etc.

c- Synthetic polymers:

Those are diverse synthetic polymers for instance synthetic fibers (nylon 6, 6), synthetic rubbers (Buna - S) and plastic (polyethylene) which are hand-made polymers widely utilized in everyday life and in industry.

2-2-2 Classification Based on Structure of Polymers:

According to the structure of the polymers, there are three different types as shown in figure (2-1)

a- Linear polymers

They consist of straight long chains, like polyvinyl chloride (PVC), high density polythene (HDPE), etc.

b- Branched chain polymers

They consist of linear chains that own few branches, like (LDPE), Low density polythene

c- Cross linked or Network polymers

They are commonly composed of tri-functional and bi-functional monomers and have strong covalent bonds between different linear polymer chains, like Bakelite, melamine, etcetera.

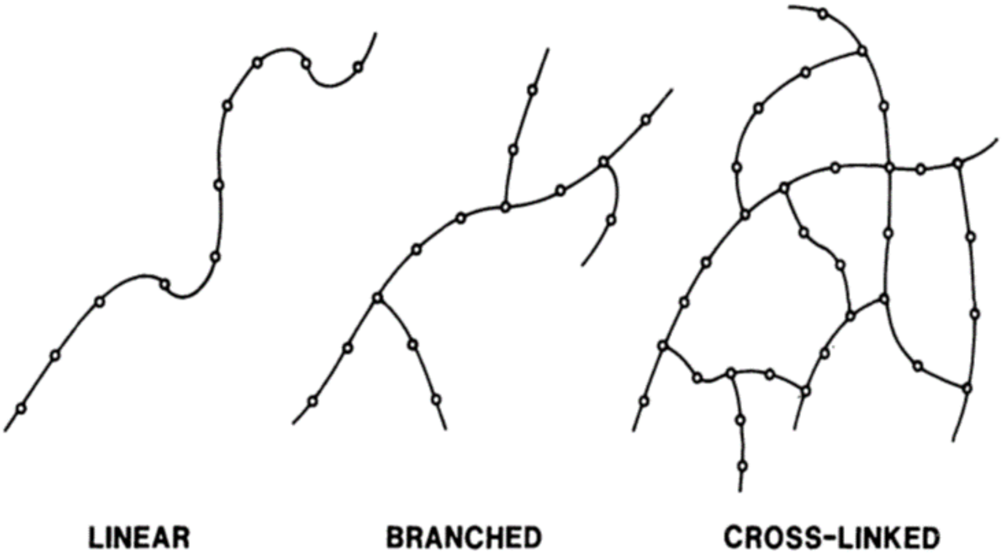


Figure (2-1) some patterns of polymers based on the chain forms

2-2-3 Classification Based on the Mode of Polymerization:

Depending on the mode of polymerization Polymers can be classified into two subgroups:

a- Addition Polymers

The frequent addition of monomeric molecules possessing double or triple bonds forms addition polymers like the formation of polythene from ethene and polypropene from propene. Moreover, addition polymers formed by polymerization of a single monomeric gender are known as homopolymers like polythene, whereas polymers made by addition of polymerization from two various monomers are termed as copolymers, like Buna S, Buna N.

b- Condensation Polymers

Repeated condensation reactions between two various bi-functional or tri-functional monomeric units form this kind of polymers. During these reactions small molecules like; hydrogen chloride, alcohol, water are eliminated, paradigms are nylon 6 and nylon 6, 6, etc.

2-2-4 Classification Based on Thermal Behavior:

Based on thermal (Thermomechanical) response which is the most useful; polymers can be classified into:

a- Thermoplastic Polymers

These polymers flow and soften by the effect of pressure and heat. By means of cooling, polymers harden and assume the shape of the mold (container). Thermoplastics usually withstand many of these cooling and heating periods without suffering any structural collapse when compounded with appropriate ingredients, for instance; PTFE, nylon polyethylene and polystyrene.

b- Thermosetting Polymers

Those are polymers that undergo chemical changes to manufacture a cross linked, solid polymer when heated. They are found initially as liquids called pre-polymers by the application of pressure and heat. They are capable of being shaped as requested but they are unable to undergo frequent periods of hardening and softening, for instance; urea formaldehyde, epoxies and phenol formaldehyde.

c- Elastomers

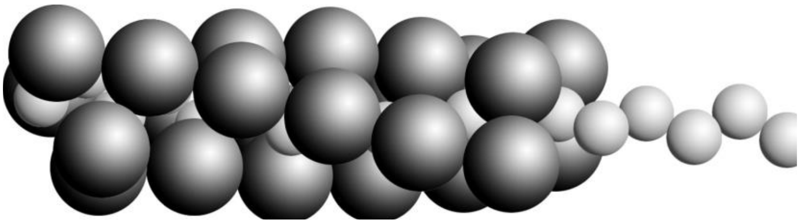
Those are rubber like solids with elastic characteristic; their polymeric chains are connected by the weakest intermolecular forces which allow the polymer to be stretchable. Some ‘cross links’ are existing amongst the chains to assist the polymer to go back to its original place after releasing the forces such as in vulcanized rubber like; neoprene.

2.3 Fluorocarbons:

This polymeric gender is differentiated by fluorine substitution, which is characterized by electrical, chemical and thermal characteristic and has four main structural classes.

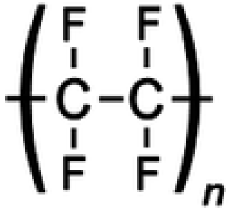
(PTFE) is a simple fluorocarbonic polymer created by polymerization of tetrafluoroethylene (TFE) ($-CF_2-CF_2-$) groups repeated endlessly. The main properties of fluoropolymers developed from the atomic structure of carbon and fluorine and their specific chemical structures in which they bond covalently to each another. (Carbon-carbon) bonds compose the backbone and the pendant groups are (Carbon-Fluorine) bonds. Both are highly strong links. The even distribution of fluorine atoms makes it non-reactive and non-polar. Poly (tetrafluoroethylene) is extremely inert and thermally stable due to its criteria of strong bonding, the non-polarity, and protective sheathing.

PTFE is a synthetic fluoropolymer known commercially and used in many industrial applications. It is often referred to by its trademark name (Teflon) which is the preferred familiar material and is non-stick and has an extremely low friction coefficient. These materials are nonflammable, nontoxic and inert; they also have good electrical properties. They are perhaps glass filled to increase rigidity and strength. They must be formed by sintering powders and they do not melt. Applications consist of mechanical, chemical, and electrical components, tubing, bearings, and vessels for chemicals [33, 34, and 35].



Large Molecule =Carbon

Small Molecule= Fluorine



$$-\!\left(\begin{matrix} F & & F \\ | & & | \\ C & - & C \\ | & & | \\ F & & F \end{matrix}\right)_{n}\!-$$

Figure (2-2) Chemical structure of polytetrafluoroethylene (PTFE).

2-4 Principle of Powder Diffraction:

It is a scientific technique that uses X-ray, electron or neutron diffraction on powder or microcrystalline specimens to characterize materials structurally.

Powder diffraction is one of the primary techniques used for material characterization; it provides structural information even when the size of the crystallite is quite tiny for a single crystal (XRD) method. In recent years there has been a significant development in the application of powder diffraction both in manufacture and research boosted by progressed instrumentation, consciousness and data processing of the obtained information. This technique allows nondestructive and rapid analysis of multicomponent mixtures without the necessity to prepare the specimens thoroughly. This enables laboratories to perform material characterization and quickly analyze unknown materials in fields such as chemistry, materials science, mineralogy, geology, archaeology, forensics, pharmaceutical sciences and biological. Great advantages of this technique are:-

- Rapidity of measurement; collection times can be very short, since all possible crystal orientations are measured simultaneously. It is one of the most powerful methods to characterize and identify new materials.
- Simplicity of specimen preparation: many materials are readily available for this technique. [36-39].

2-5 Polymers and Plastics:

The terms ‘polymers’ and ‘plastics’ are usually synonyms but actually they are distinct. Polymers are pure materials result from the polymerization process and are commonly used as the family name for materials possessing long chain like molecules and this includes rubbers. Pure polymers are rarely used independently; the term plastic is applied when the additives exist. Polymers have additives for several purposes. The list below resumes the reasons of essential additives used in plastics.

Fillers: the mechanical properties of plastic are improved by some fillers like short fibers or flakes of inorganic materials.

Extenders: they permit the production of massive volume of plastic with comparatively little actual resin. Clay, calcium carbonate and silica are commonly utilized extenders.

Lubricants: such as calcium stearates or wax improve forming properties and reduce the molten plastic viscosity.

Pigments: they are utilized to produce color plastics.

Stabilizers: they prevent plastic deterioration by environmental factors, such as heat stabilizers; they are required in processing polyvinyl chloride. Stabilizers also prohibit the harmful effect of the ultraviolet radiation on plastics [40, 41].

2-6 Crystallinity:

The degree of structural order in a solid is referred to as crystallinity. Molecules or atoms are organized in a periodic manner, uniform in the crystal. The crystallinity degree affects majorly the hardness, density, diffusion, transparency. Crystallinity may be detected by diffraction techniques, heat-of-fusion measurements, etc. [42]

The mechanical and physical characteristics of semi crystalline thermoplastic polymers rely on the orientation apportionment of the crystalline volume portion and on the degree of crystallinity. These quantities usually change when the specimen is exposed to mechanical and thermal loads. This indicates that the orientation distribution and the degree of crystallinity are history dependent features in these materials.

The degree of crystallinity can be determined by several experimental techniques including X-ray diffraction (XRD), differential scanning calorimetry (DSC) the various techniques may be affected by different extents by imperfections and interfacial effects[43,44].

2-6-1 by x-ray diffraction

To determine the crystallinity degree, several x-ray diffraction methods are stated and worked out.

a- Separation of overlapping peaks method applied by Hineleh and Sh.M.Abdo (1989) for synthetic polymers are successful to identify the crystallinity especially in cases of possession of polymer preferred orientation or texture.

In this method, it requires quantization crystalline to separate the distribution of intensity of peaks of the crystalline areas and the distribution of intensity of the amorphous area and background intensity in addition to conducting intensity corrected from the effect of polarization and Lorenz factor [45].

Depending on Gauss function to separate the peaks to calculate the intensity I_{cal} from equation:

$$I_{cal} = \sum_{t=1}^{n} G_t = \sum A_t \exp[-\ln 2[\frac{(2(X_t - P_t)}{\omega_t}]^2] \ldots\ldots. (2\text{-}1)$$

Where:

X_t: Angle 2Θ.

A_t: Peak height.

P_t: Angular location of top peak.

n: Number of height peaks calculated.

The crystallinity X_c is a structural formula as the ratio between the scattering of the totally separated peaks to total scattering under the form side of the spectrum at a specified angular range after subtracting background intensity and would be as following: [46].

$$X_c = \frac{\sum_{t=1}^{B}\int_{2\theta_1}^{2\theta_2} I_t\,(2\theta)d(2\theta)}{\int_{2\theta_1}^{2\theta_2} I_{nor}\,(2\theta)d(2\theta)} \text{ …….. (2-2)}$$

Where:

I_t (2Θ): totally scattering for separated peaks in the spectrum.

I_{nor} (2Θ): totally scattering for spectrum.

$2\Theta_2$-$2\Theta_1$: angular range chosen.

B: number of separated peaks in spectrum.

b- (WAXD) Wide angle X-ray diffraction method is the most common. The intensity of x-ray scattered from the entire specimen is the entire area under the diffraction pattern. There are two zones of total intensity; amorphous and crystalline. Intensity of diffracted beam from amorphous part (I_a) is the remaining area under the curve above background and intensity of diffracted beam from crystalline part (I_C) is the area under the sharply peaks [47].

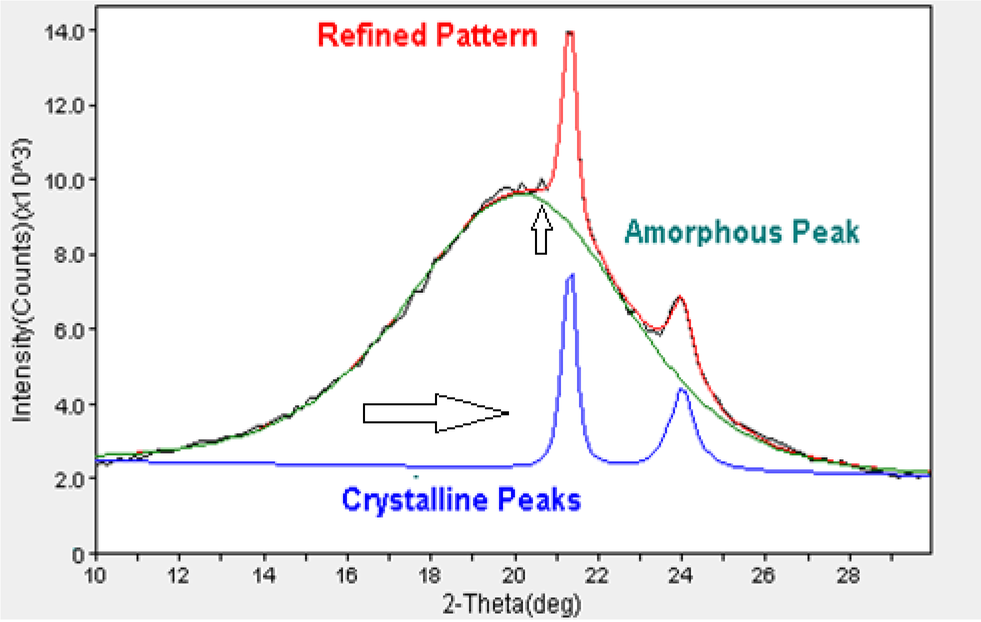


Fig. (2-3) shows the crystalline and amorphous regions.

Thus the crystallinity degree is calculated by this equation;

$$X_C\ \% = \frac{Ic}{Ic+Ia} \ldots\ldots (2\text{-}3)$$

$$X_C\ \% = 1 + \frac{Ic}{Ia} \ldots\ldots\ (2\text{-}4)$$

$$X_C\ \% = (1+\frac{Ia}{Ic})^{-1} \ldots\ldots\ (2\text{-}5)$$

Where:

X_C: Is the crystallinity of polymer.

I_C: Intensity of crystalline region.

$I_{a:}$ Intensity of amorphous region.

This method is superior to the conventional intensity minimum line structure method. In contemporary equipment, (WAXD) data is of adequately high-quality but curve fitting is more effective, for this aim long count times or sufficiently slow angular scan speed are preferred. [48]

2-6-2 By Differential Scanning Calorimetry:

This method is based on measuring the heat content (Enthalpy) of the model. This instrument is engineered to measure the amount of heat evolved or absorbed from a sample under isothermal conditions. (DSC) includes two pans; one reference pan that has a polymer specimen and another pan which is empty. The polymer specimen in this method is heated with reference to a reference pan. Both polymer and reference pan are heated at the same rate. The quantity of excess heat absorbed by a polymer specimen is with reference to reference material.

(Dole) gave expression to determine the degree of crystallinity for polymeric material by Relevancy [49, 50].

$$X_c\% = \frac{\Delta H}{\Delta H^{\circ}} * 100\,\% \ldots\ldots \text{(2-6)}$$

Where:

ΔH : The quantity of Enthalpy melting of the sample .

ΔH° : The quantity of Enthalpy melting of the sample totally crystalline.

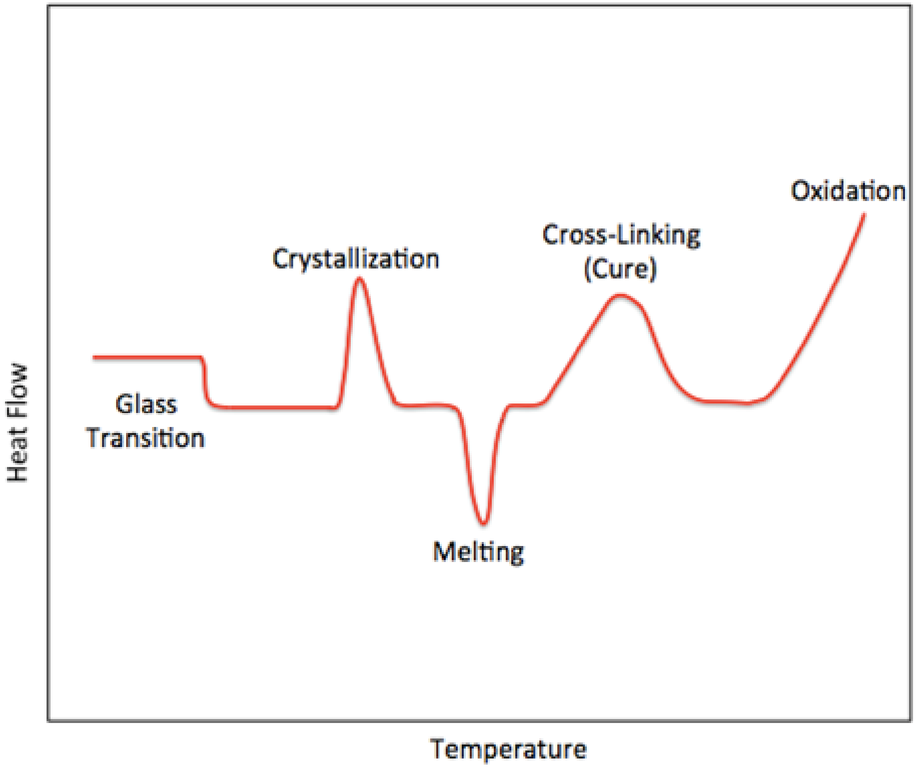


Figure (2-4) The curve line DSC and example of physical processes occurring while heating the sample.

2.7 Mechanical Properties

They are the characteristics exhibited by the material when subjected to externally applied mechanical force. In other term, mechanical properties speak about the reaction of a material to applied forces [51].

2.6.1 Tensile Test:

It is a common test, by using the properties obtained; it can be applied to design several components. Tensile test arranges the resistance of materials to static forces or slowly applied. The strain rates in a tensile test are commonly minimum [52].

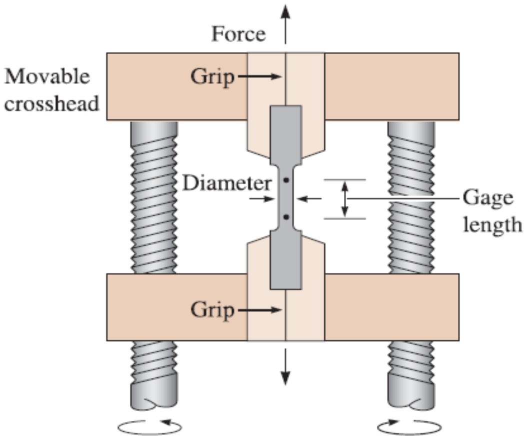


Fig. (2-5) unidirectional force used to a sample in tensile test [53].

The stress–strain tests make the sample deformed (pulled) at a stable rate; the stress required for this deformation is measured simultaneously. In this test the buildup of a force or stress is measured as the sample is being deformed at a stable rate [54].

Generally, the stress is the acting force per unit area over which the force is applied. We can be defined Strain as the change in dimension per unit length. Strain has no dimensions and stress is usually expressed in Pascals (Pa) [55].

The stress over the circular cross section that is perpendicular to the axial load will be: $\boldsymbol{s} = \frac{\mathbf{F}}{\mathbf{A}}$ …… (2-7)

Where *F is* the force applied and A is cross-sectional area

Strain = $\frac{\Delta \boldsymbol{L}}{\boldsymbol{L}}$…… (2-8)

Where L is the original length and ΔL is the change in length [56].

Stress acquired at the highest applied force is called Tensile strength which is the maximum stress on the engineering stress strain curve. This amount is usually known as the ultimate tensile strength. At some point, one region is deformed more than others and a large, local decrease in the cross sectional area occurs. This locally deformed region is called the neck and this state is called necking. At this point a lower force is desired to continue its deformation due to smaller cross-sectional area, the engineering stress, determined from the original area A [52].

Young's modulus (*E*) or the modulus of elasticity is the slope of the stress strain curve in the elastic region. Hooke's Law is the relationship between stress and strain in the elastic region is known [57, 58].

$\boldsymbol{E} = \frac{\boldsymbol{stress}}{\boldsymbol{strain}}$**….** (2-9)

The slope of the tensile stress-strain curve in the elastic portion is defined as Young's modulus (*E*) or the modulus of elasticity of a material see fig. (2-6) the units of *E* are measured in Pascals (Pa) or in pounds per square inch (psi), same as those of stress. The application of load correlates with moving up alongside the straight line from the origin. By releasing the load, the line turns back in the opposite direction to its origin [59, 60].

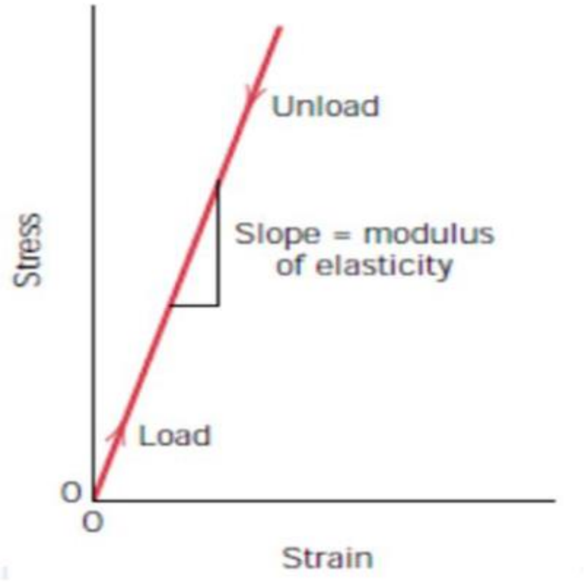
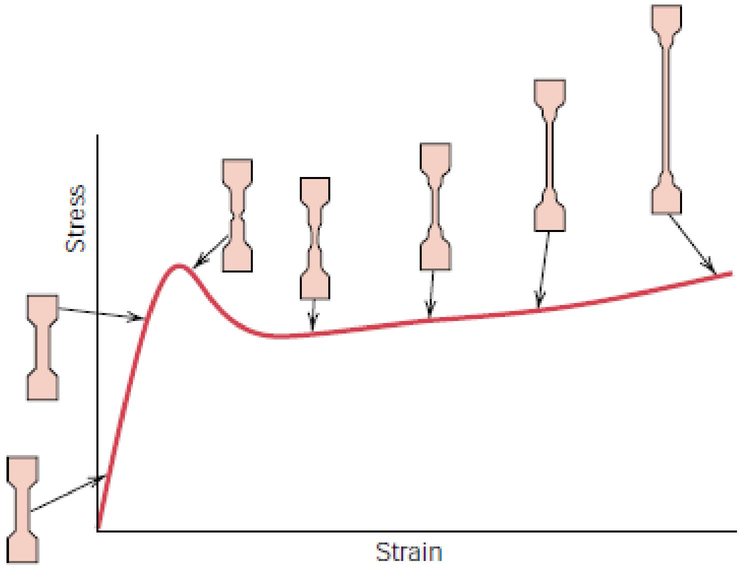


Figure (2-6) graphic stress-strain diagram shows linear elastic Deformation for unloading and loading cycles [61].

In a material, the plastic deformation is called the plastic strain. By these status, when removing stress, the material doesn't return to its original shape. A dent in a car is plastic deformation. Notice that the word “plastic” here does not indicate strain in plastic (polymeric) materials, but rather indicates a permanent strain in any material (Fig. (2-7)) [62].



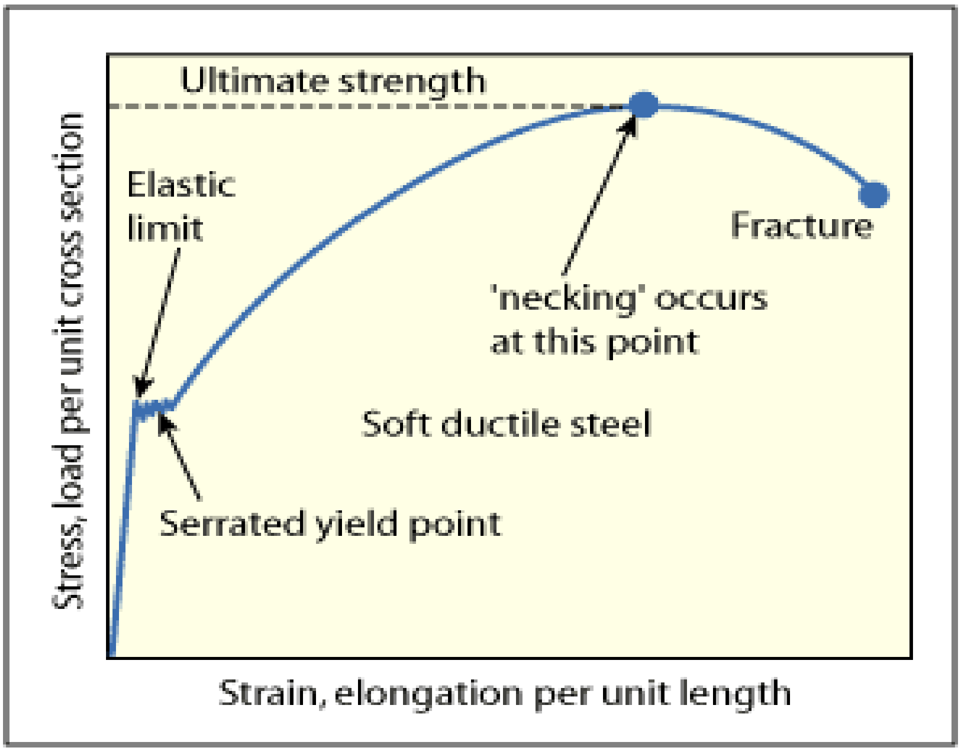


Fig. (2-7) Schematic tensile stress–strain curve for a semi-crystalline polymer. Specimen contours at several stages of deformation are included [61].

3-1 Samples used

We used two sets samples of PTFE ribbon with different origins for all set 30 samples.

-The first set is a ribbon of polymer (PTFE) China origin.

-The second set is also a ribbon of (PTFE) but Emirates origin.

The first and second sets differ in their thickness and possess the same intensity

Table (3-1) PTFE ribbon with different origins or manufacturing

NO	**Origin**	**Manufacturer**	**Thickness (mm)**	**Width (cm)**	**Density (g/cm^3)**
1	China	Profish-city	0.25	1.9	0.3
2	Emirates	United company	0.1	1.9	0.35

By taking the bar, it is made of this article polymeric that was prepared from solution cast as film and strip, it has been preparing the two sets of samples in the form of a rectangular shape dimensions (14×1.9) cm.

3-2 Thermal treatment:

Samples were treated in a (Carbolite chamber furnaces with maximum operating temperatures 1200°C). Thermally it was put in a non-vacuum furnace for 30 minutes in a free way of the shrinkages and in temperatures (Rt, 100, 200, and 250) °C each set separately. The samples were prepared for structural and mechanical tests.

3-3 Powder Diffractometer

Using X-ray diffraction system for powder diffraction for diffraction spectra of the samples for high accuracy advantage in step scan to measure Bragg's angle and the intensities associated with angles sites by counters to record the reflections from crystalline levels shown on computer by a special program.

This technology has been worked on through X-ray diffraction device type (SHIMADZU Japan) (XRD600), and the following specifications:

Wavelength	1.5418 A
Radiation	CuKα1
Current	30 mA
Voltage	40 kv
Range	(10-70) deg
Speed	8deg /min

Four samples were tested for each group in varying heat treatment

(RT, 100,200, and 250) °C.

3-4 Differential Scanning Calorimetry (DSC):

This system (Linseis company-Germany) records curves of heat content as a function of temperature by Using two small crucible made of a material alumina, one of a substance reference and the second is often remained empty for the sample to be examined, the PTFE samples weight were about (10 mg). Samples were pressured to small size to accommodate examination crucible and to raise the temperature of the furnace at a rate of 25°C which the temperature of the laboratory to 450 °C by passing N_2 gas inside the furnace.

The two crucibles contain a running thermal Picker and link holder to the sensor, which is a thermocouple senses the difference in temperature between the sample and the material reference and has been linked to a computer to record the change in temperature as a function of time and turn it into a thermal flow in the form of a signal which is recorded and drawn in the form of curved computer screen within a specific program in which the time rate of heat flow is shown as a function of temperature.

And it works them out on a differential curve in which energies are absorbed peaks towards the top and clarified bottom refers to chemical reactions, physical properties and transitions taking place in the sample. The process is repeated to the second sample too.

These furnaces are specially designed to allow fast cooling and heating rates, moreover to precisely high temperature control. This system can be optionally equipped with a coupling device for evolved gas analyses (EGA).This device is highly suitable for thermal stability, oxidation studies and thermal composition.

3-5 Mechanical Property Test

The mechanical test is important to identify the mechanical properties of polymers by appointing stress-strain and Young modulus.

The behavior of tensile samples was marked at room temperature by utilizing tensile testing instrument model (H50KT) produced by (Tinius Olsen / UK). Samples were prepared as figure (3-5)

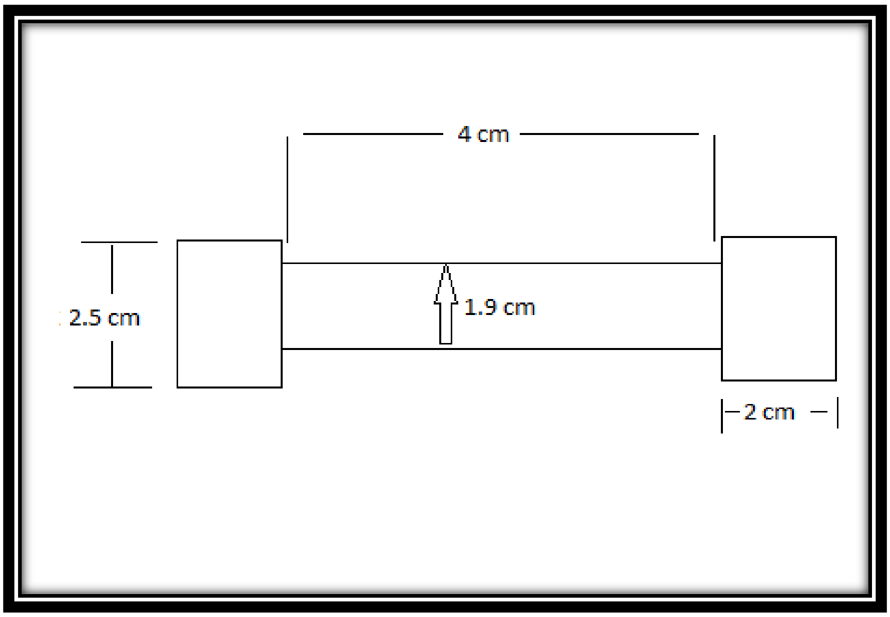


Figure (3-5) Planner for the dimensions of sample examination

The specimen was loaded at speed 5 mm/min between two grips adjusted by hand for (2000 N) computerized tensile test instrument, with an electronic expansion. Load-Elongation curves were recorded and yield stress and strain were calculated at the corresponding points to the Load-Elongation curve, we also calculate the amount of strain by identifying the difference between primary and final lengths occurring in process of drag when cutting the sample and determine the Young modulus depending on the linear part of the stress-strain curve.

Each test was repeated for each of the sets (RT, 100, 200, and 250 ˚C) to calculate the tensile properties of the samples.

(4-1) Crystallinity

(4-1-1) the Degree of Crystallinity from X-ray Diffraction (XRD)

Figure (4-1) shows the diffraction spectra X-radiation scanned the angular extent of (10°-70°) samples untreated and heat treatment at different temperatures between (RT - 250) °C.

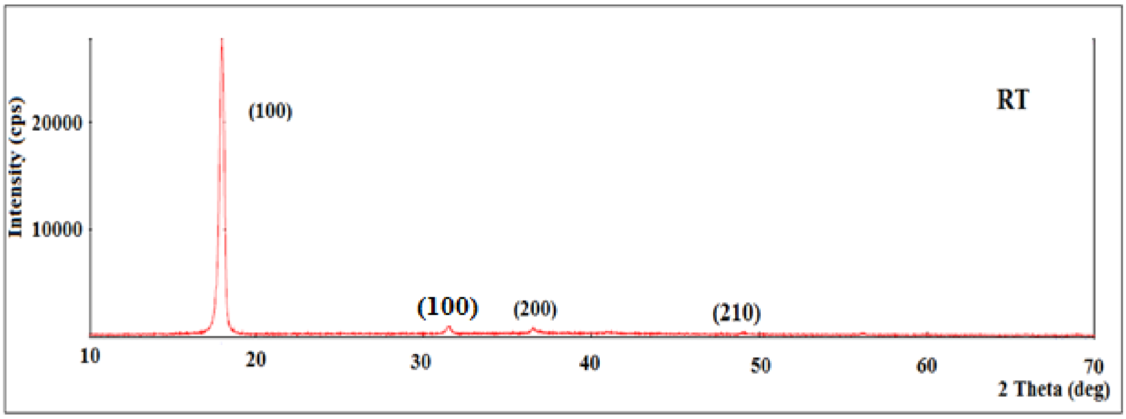
The careful analysis of the wide angle of X-ray scattering data was performed to determine different reflections, remarkable valuable variation is recognized in the modification of intensities of different peaks withdrawn and undrawn (PTFE). As shown in X-ray diffraction patterns different peak positions are the same in every situation, and the intensities of the reflections (100,110,200,210) planes at 2θ of (18 /31/ 36/ 49) respectively.

The method of (WAXD) has been modified for the determination of crystallinity in polymers and (WAXD) has been applied in the crystal structure evaluation of poly (tetrafluoroethylene) PTFE for each type. Spectra of the polymers at four diffraction temperatures are displayed in figure (4-1) and (4-2) for two modifications of PTFE specimens respectively .The diffraction pattern did not change except for the variation in its peak rising. Four distinct peaks are observed in the spectra; the inter planer spacing equation for triclinic system [63]. As shown in table (4-1).

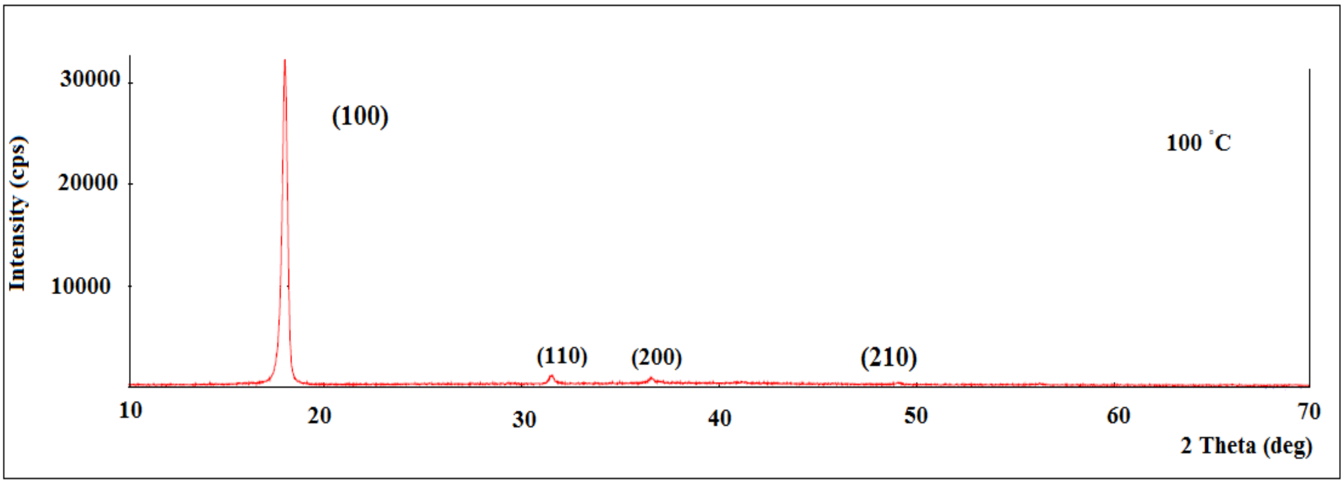
Table (4-1): Miller indices (hkl) assigned for peaks in XRD spectrum for poly (tetrafluoroethylene) PTFE.

2 θ (deg)	d obs.(nm)	d calc.(nm)	hkl
18.047	4.90	4.915	(100)
31.6	2.83	2.830	(110)
36.57	2.43	2.423	(200)
49	2.18	2.182	(210)

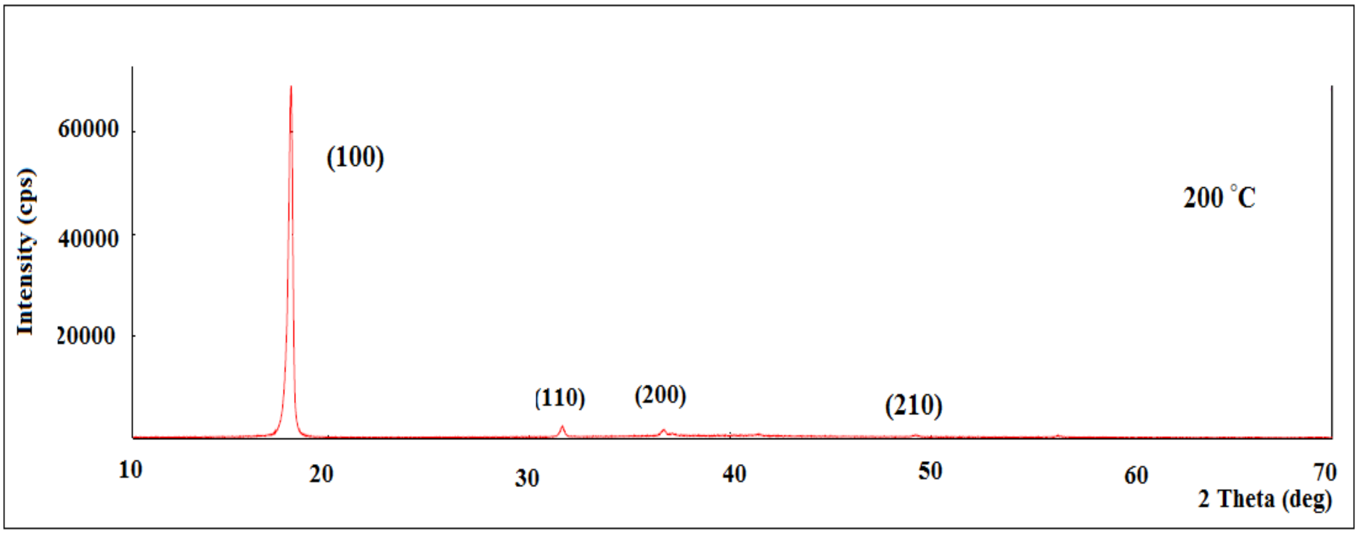
We chose the intensity of the (100) plane for its higher value of intensity than the other peaks. In this intensity the increase in the type (1) remains better than in type (2) with increasing the temperature of the heat treatment up to 250°C. This is due to possible re-orientation in the molecular chains caused by the heating cycle. on the another hand the way of preparing those two types affects the orientation of the molecular chains whereas the heating cycle increased the order of orientation chains in type (1) better than it did in type (2) that means the degree of crystallinity in type (1) is better than type (2) because of the way of preparing these types with the increase in heating cycle.



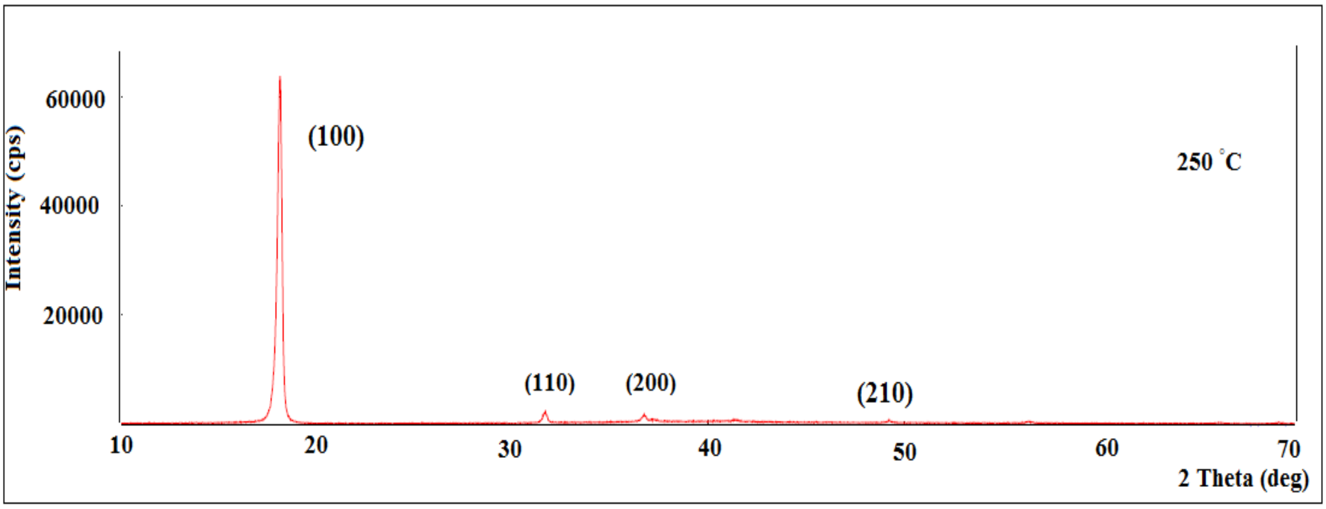
(A)


30000
20000
10000
Intensity (cps)
(100)
(110)
(200)
(210)
100 °C
10
20
30
40
50
60
70
2 Theta (deg)

(B)

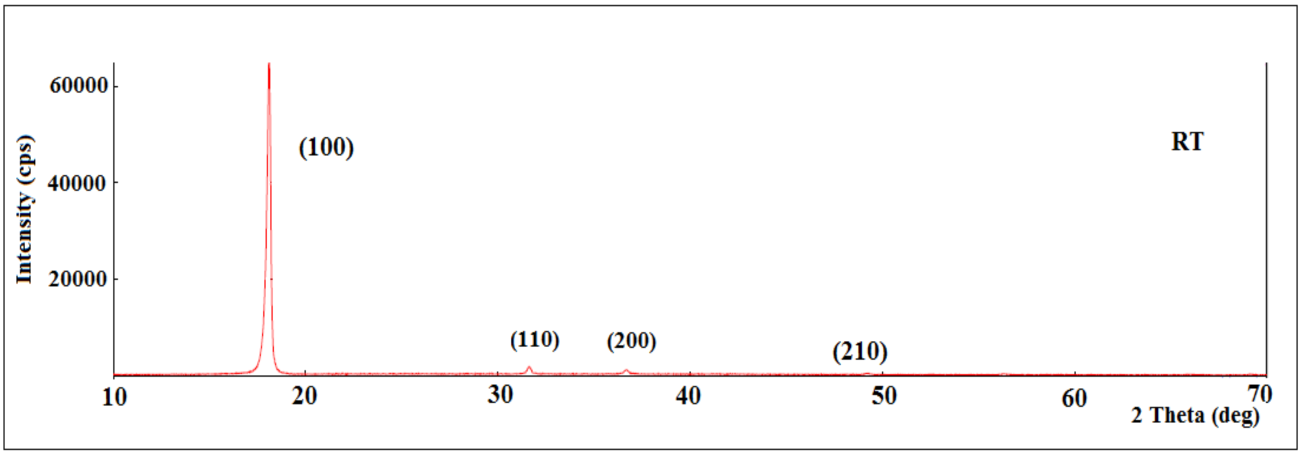

60000
40000
20000
Intensity (cps)
(100)
(110)
(200)
(210)
200 °C
10
20
30
40
50
60
70
2 Theta (deg)

(C)

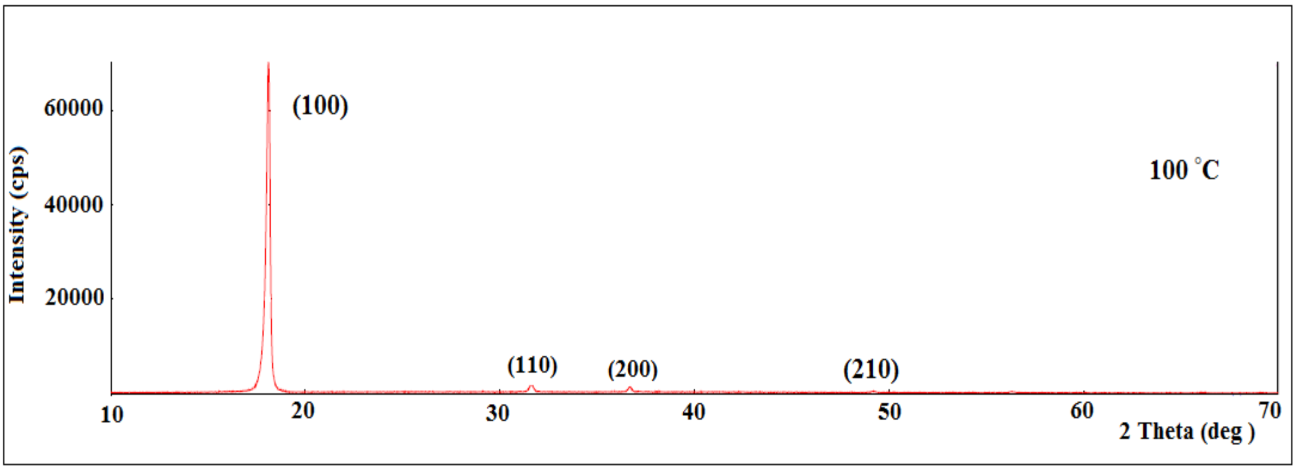


(D)

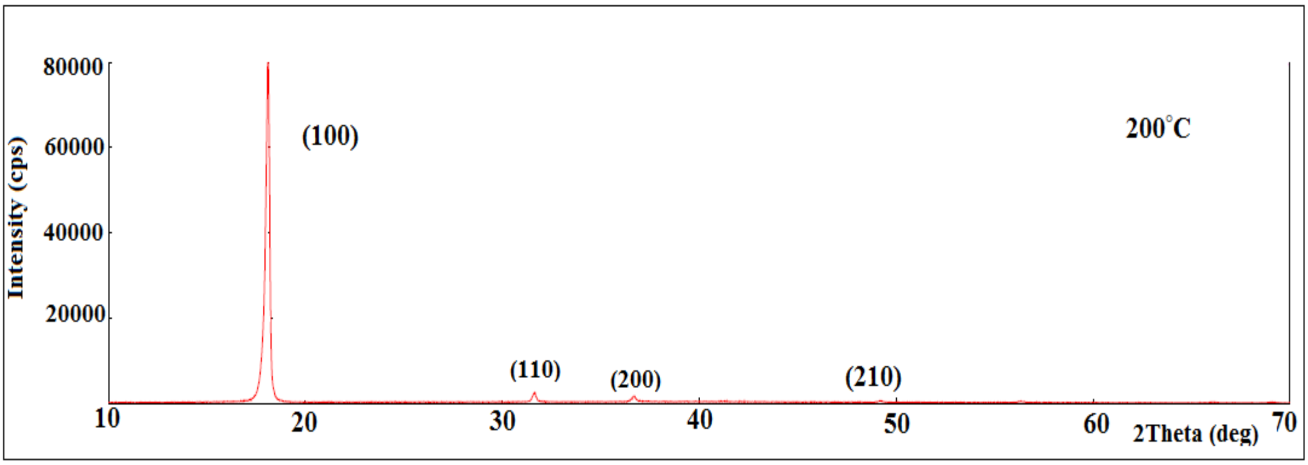
Fig. (4-1) (A-D) XRD for (PTFE) type (1) at different temperatures (RT, 100, 200, and 250) °C.



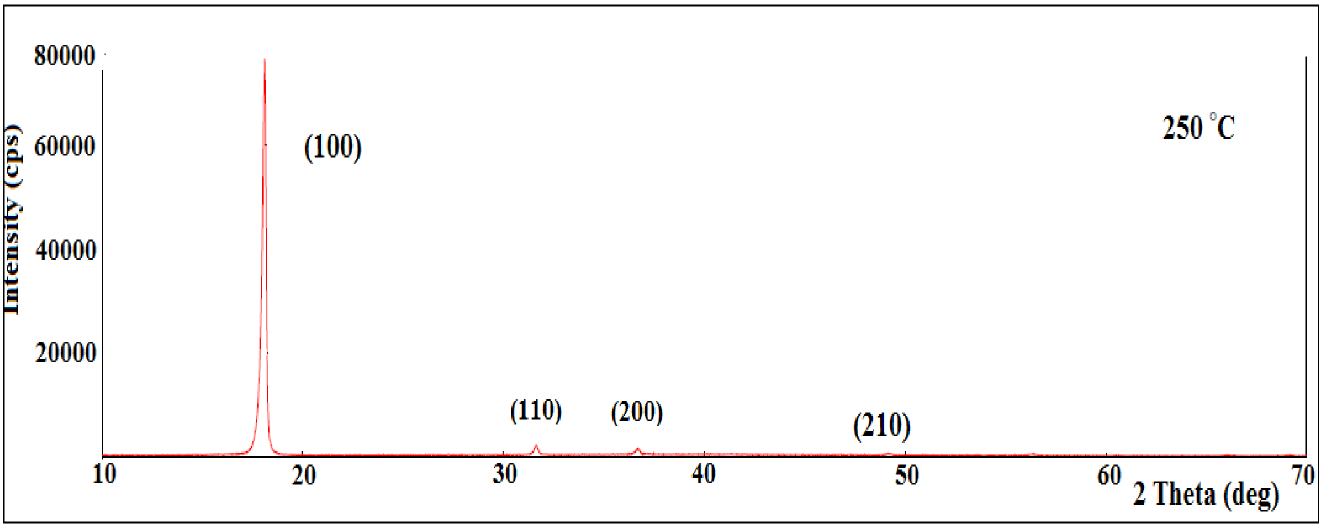
(A)



(B)



(C)



(D)

Fig. (4 -2) (A-D) XRD for (PTFE) type (2) at different temperatures (RT, 100,200, and 250) °C

Degree of crystallinity calculated from equation (5) and given in table (4 -2)

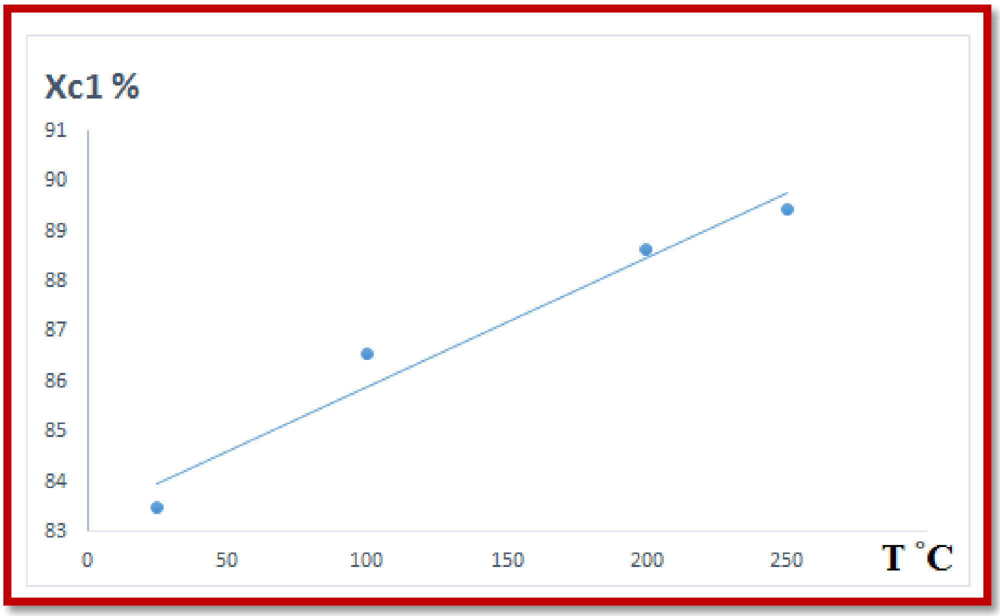
Table (4- 2) : The degree of crystallinity calculated by XRD for both types

Type	2 θ of peak (100)	T °C	X_C %
(1)	18.0315	RT	83.5
	18.0476	100	86.54
	18.1478	200	88.63
	18.1892	250	89.44
(2)	18.1344	RT	75.03
	18.1403	100	77.84
	18.1349	200	87.29
	18.1314	250	89.13

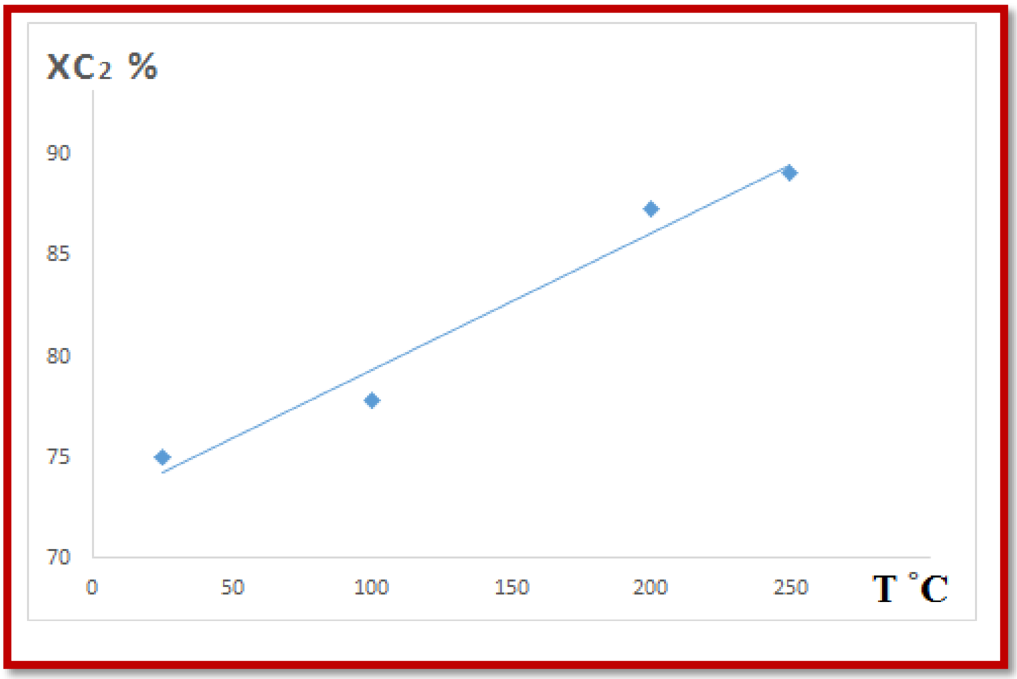
It has been noticed that type (1) is more pure than type (2) which gives it a good value for degree of crystallinity than the other.

Table (4-2) shows that a reflection position (100) increases with the increase of temperature and up to 250°C .The reason is that the sample of (PTFE) is a free shrinkage during heat treatment that leads to freedom in the movement of molecules within the crystal lattice because the sample had the highest preferred orientation in the way of manufacturing (solution cast as film and strip).PTFE except for other semi crystalline polymer (PET, PE, PP...) where there is a decrease in crystallinity during heat treatment. [64]

This shows that the increase in temperature leads to the appearance of some crystalline regions and thus the appearance of other reflection locations. The interpretation, which supports other reflections in the spectrum diffraction of the samples (110), (200) and (210)



(a)



(b)

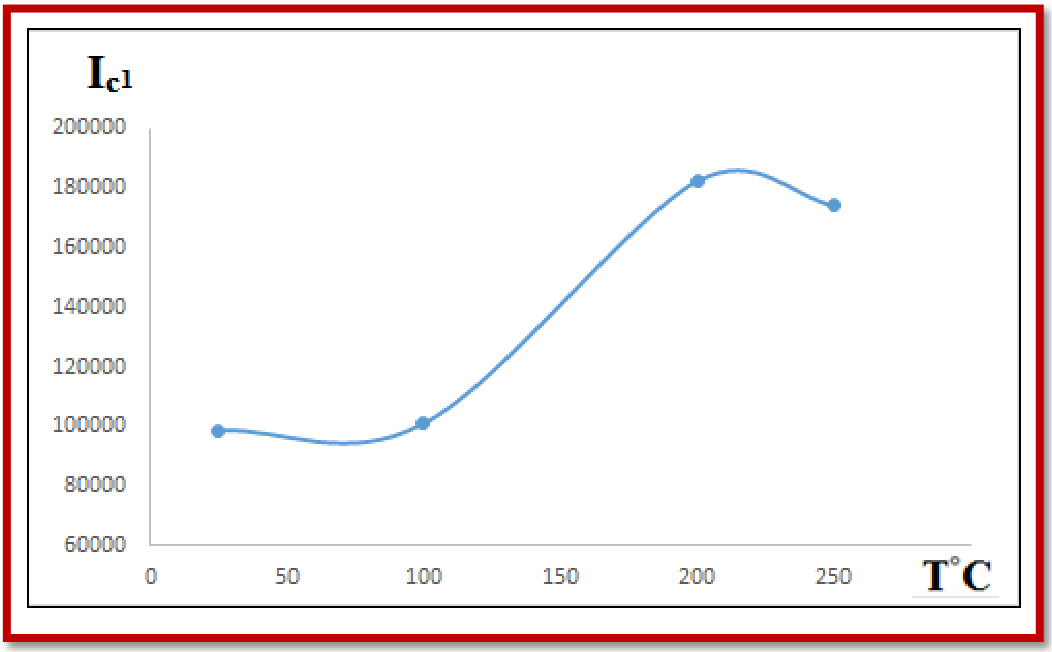
Figure (4-3) (a,b) show the difference in degrees of crystallinity between types (1) and (2) depending on the temperature.

The highest degree of crystallinity was recorded in type (1) which increases slightly from type (2) the reason due to the way of preparation of those two types effect on the orientation of the molecular chains. As shown in figure (4-3).

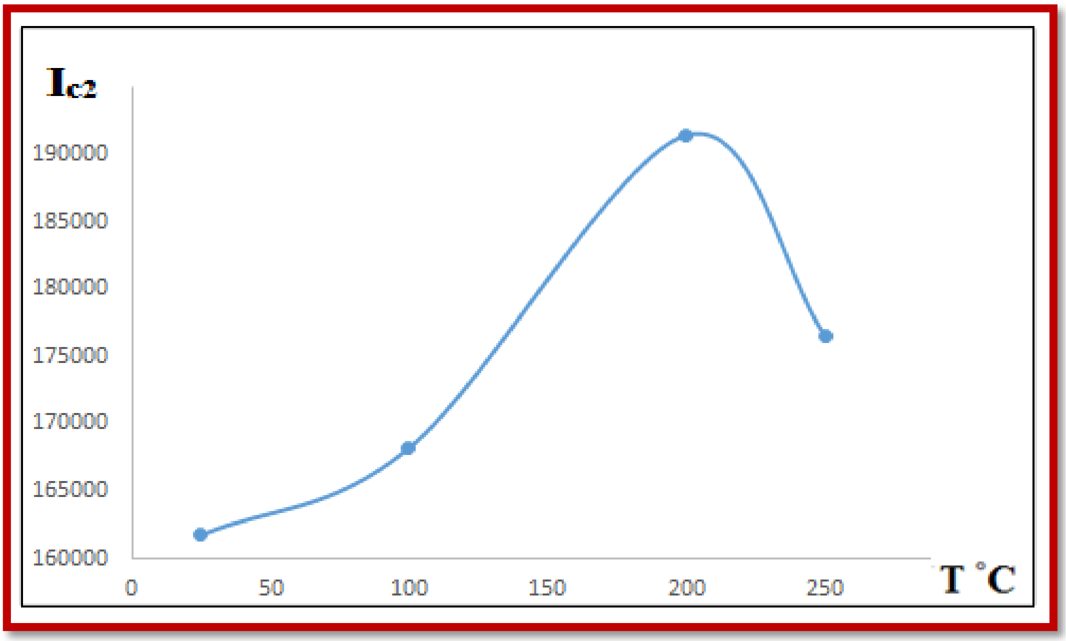
In another side and from table (4-3) we can show the increase in intensity of crystalline region for the two types as shown in figure (4-4). The crystalline region increases with the increase of temperature except for the sample with 250˚C where it has been noticed that the crystalline region started to decrease at this temperature, a decrease of peak height may mean that there is a phase transition above 200˚C or more x-ray absorbing material in the path of the x-ray beam. If the heat treatment causes oxidation of the material [65], for the same reason we can notice the increase in the amorphous region at the temperature of 250˚C while in other temperatures it is still decreasing as in figure (4-5) below. Intensity of amorphous and crystalline region for all temperatures are given in table.

Table (4-3): shows intensity of amorphous and crystalline region for two types

Type	T °C	I_c	I_a
(1)	RT	98876	9055.2
	100	101142	7287.5
	200	182458	1085.4
	250	174324	9534.8
(2)	RT	161754	24948
	100	168226	22185
	200	191460	12912
	250	176524	99715

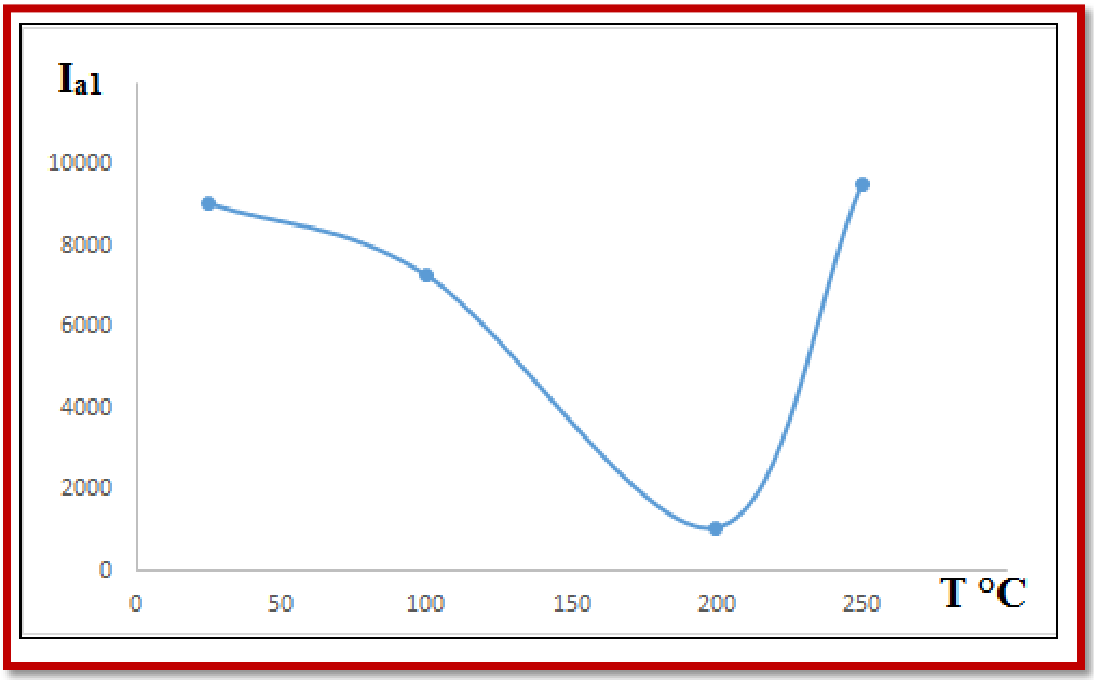


(a)

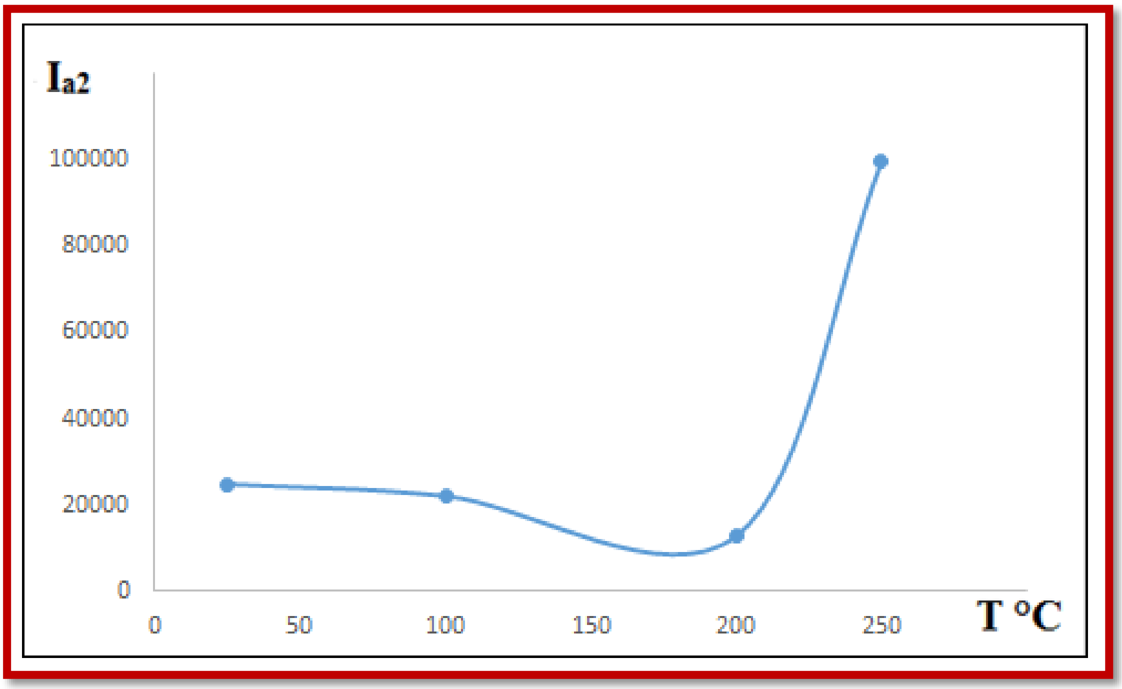


(b)

Figure (4-4) (a,b) show the increasing in crystalline region with the increase in temperature for type (1) and type (2)



(a)



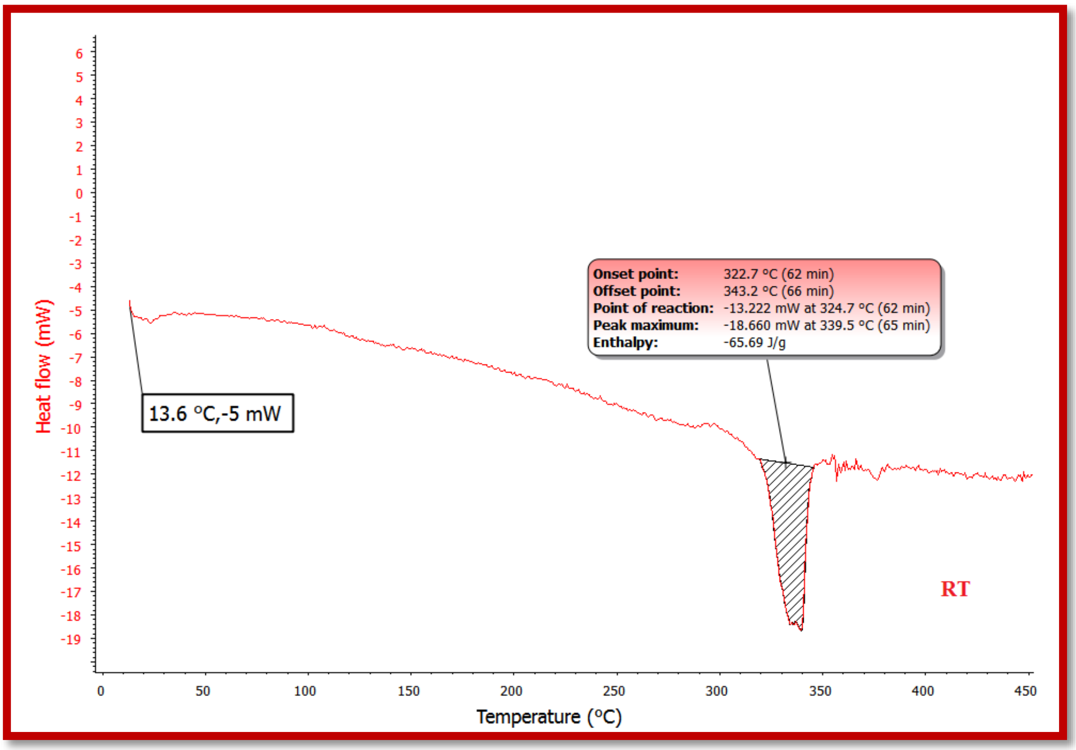
(b)

Figure (4-5) (a,b) show the decrease in amorphous region with the increase in temperature for type (1) and type (2)

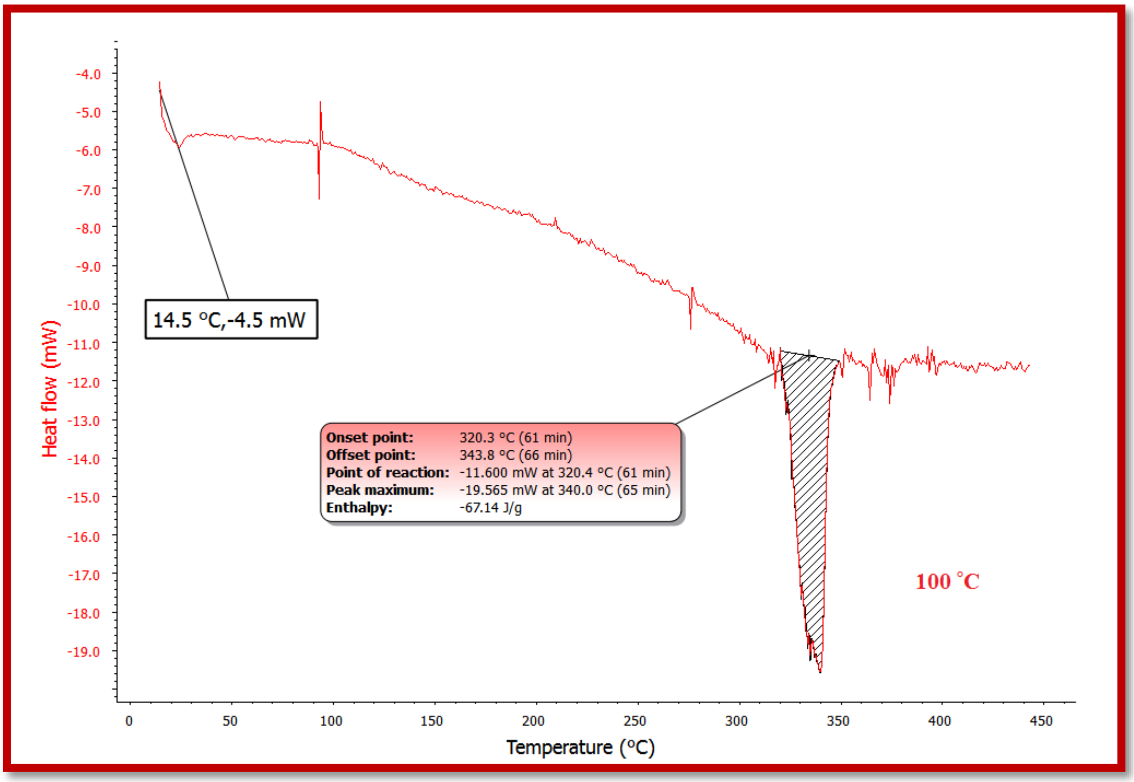
(4-1-2) The Degree of Crystallinity from (DSC)Differential Scanning Calorimetry :

Figure (4-6) and (4-7) show the heat content (enthalpy) curve a function of temperature for PTFE samples for two types. Where changes has been observed in the tendency of curve at (115 ˚**C**) represented as glass transition degree and existence of a peak endothermic at (330˚**C**) [66] represented as melting point of polymer.

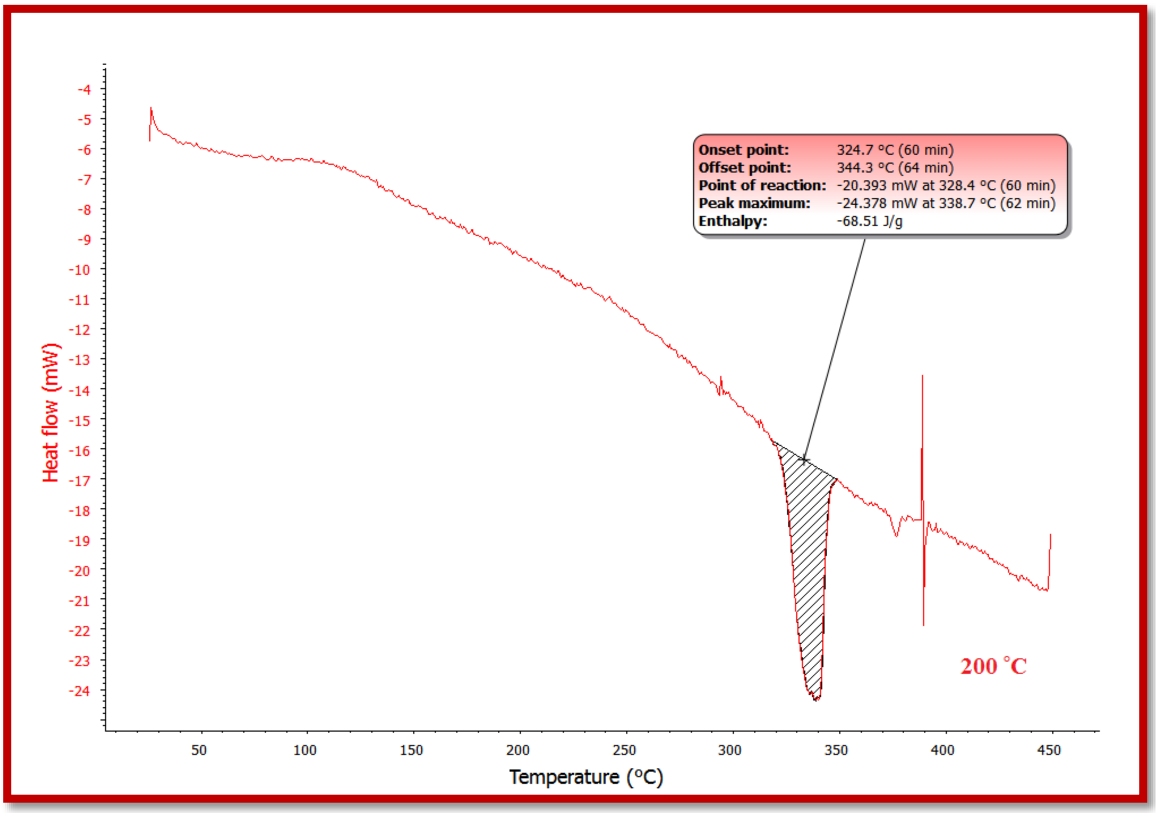
The thermal behavior for the two types of polymer is similar with some differences in the glass transition and melting point because of the nature of the sample and the way formed.



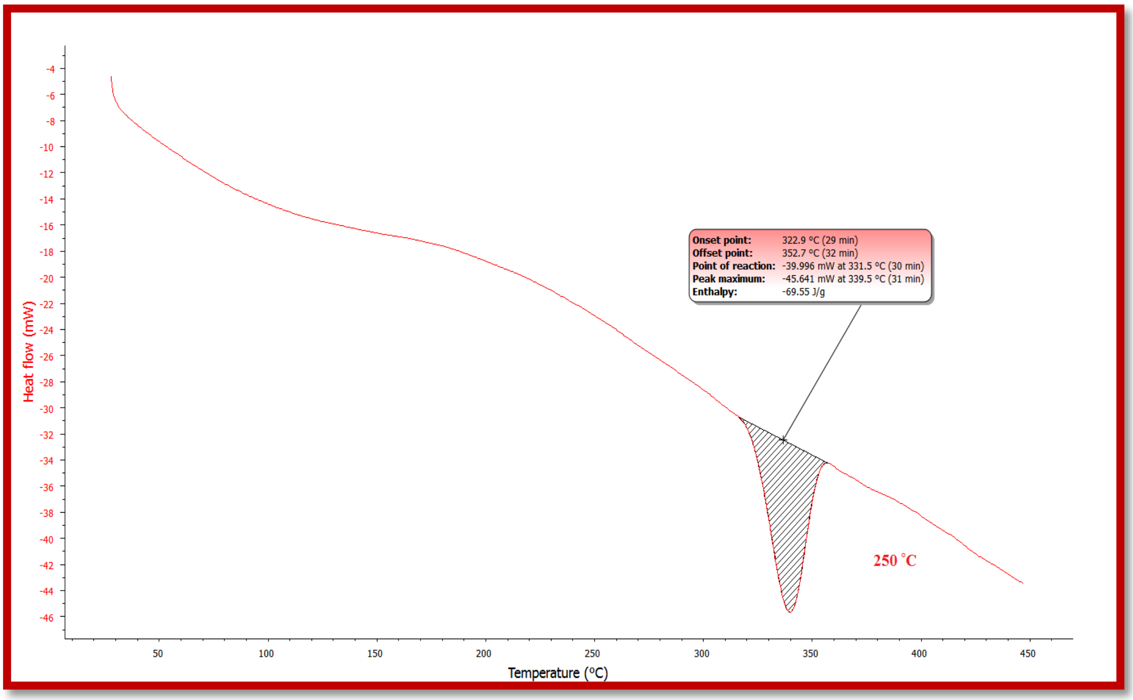
(A)


Heat flow (mW)
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
-12.0
-13.0
-14.0
-15.0
-16.0
-17.0
-18.0
-19.0
14.5 °C,-4.5 mW
Onset point: 320.3 °C (61 min)
Offset point: 343.8 °C (66 min)
Point of reaction: -11.600 mW at 320.4 °C (61 min)
Peak maximum: -19.565 mW at 340.0 °C (65 min)
Enthalpy: -67.14 J/g
100 °C
0
50
100
150
200
250
300
350
400
450
Temperature (°C)

(B)


Heat flow (mW)
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
-15
-16
-17
-18
-19
-20
-21
-22
-23
-24
Onset point: 324.7 °C (60 min)
Offset point: 344.3 °C (64 min)
Point of reaction: -20.393 mW at 328.4 °C (60 min)
Peak maximum: -24.378 mW at 338.7 °C (62 min)
Enthalpy: -68.51 J/g
200 °C
50
100
150
200
250
300
350
400
450
Temperature (°C)

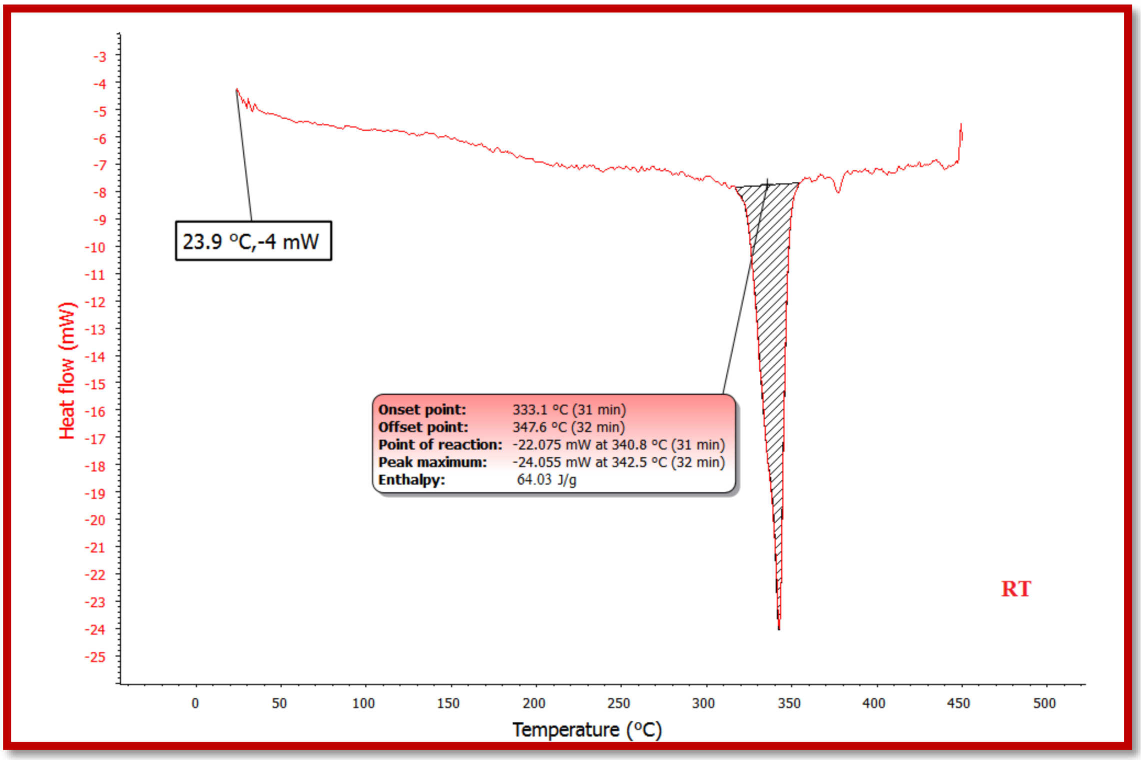
(C)



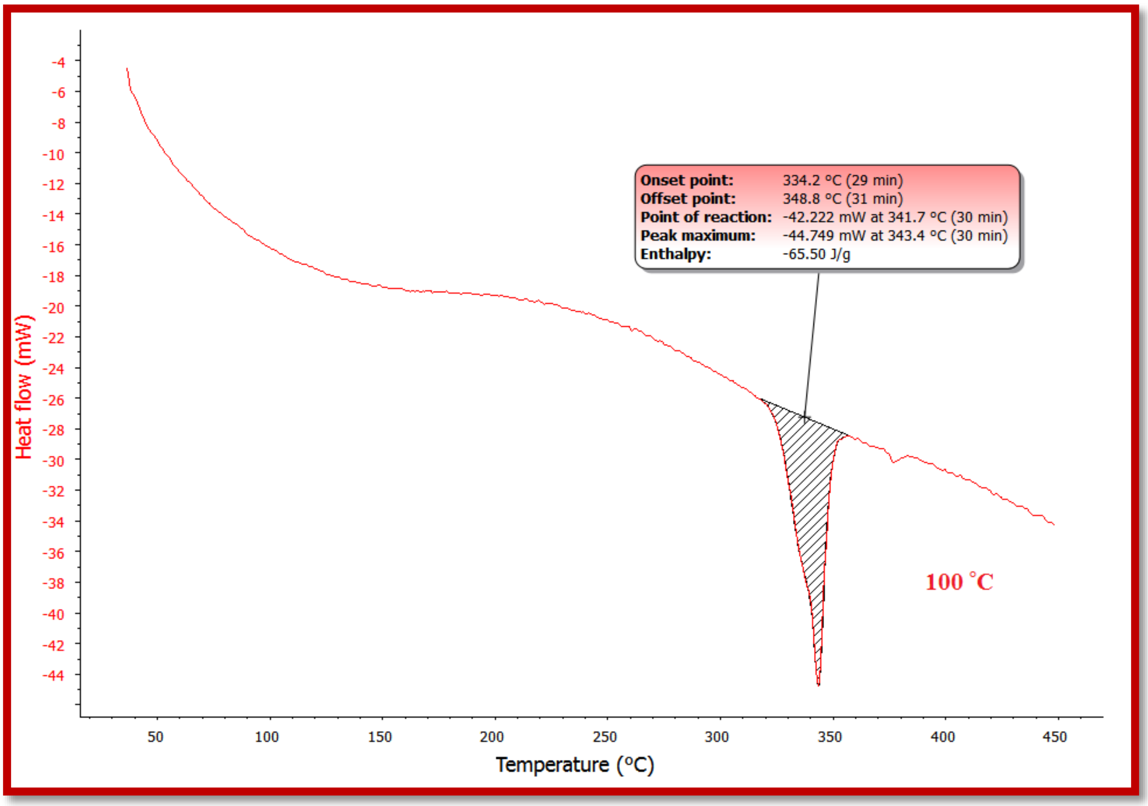
(D)

Fig. (4 -6) (A-D) the heat content function to temperature

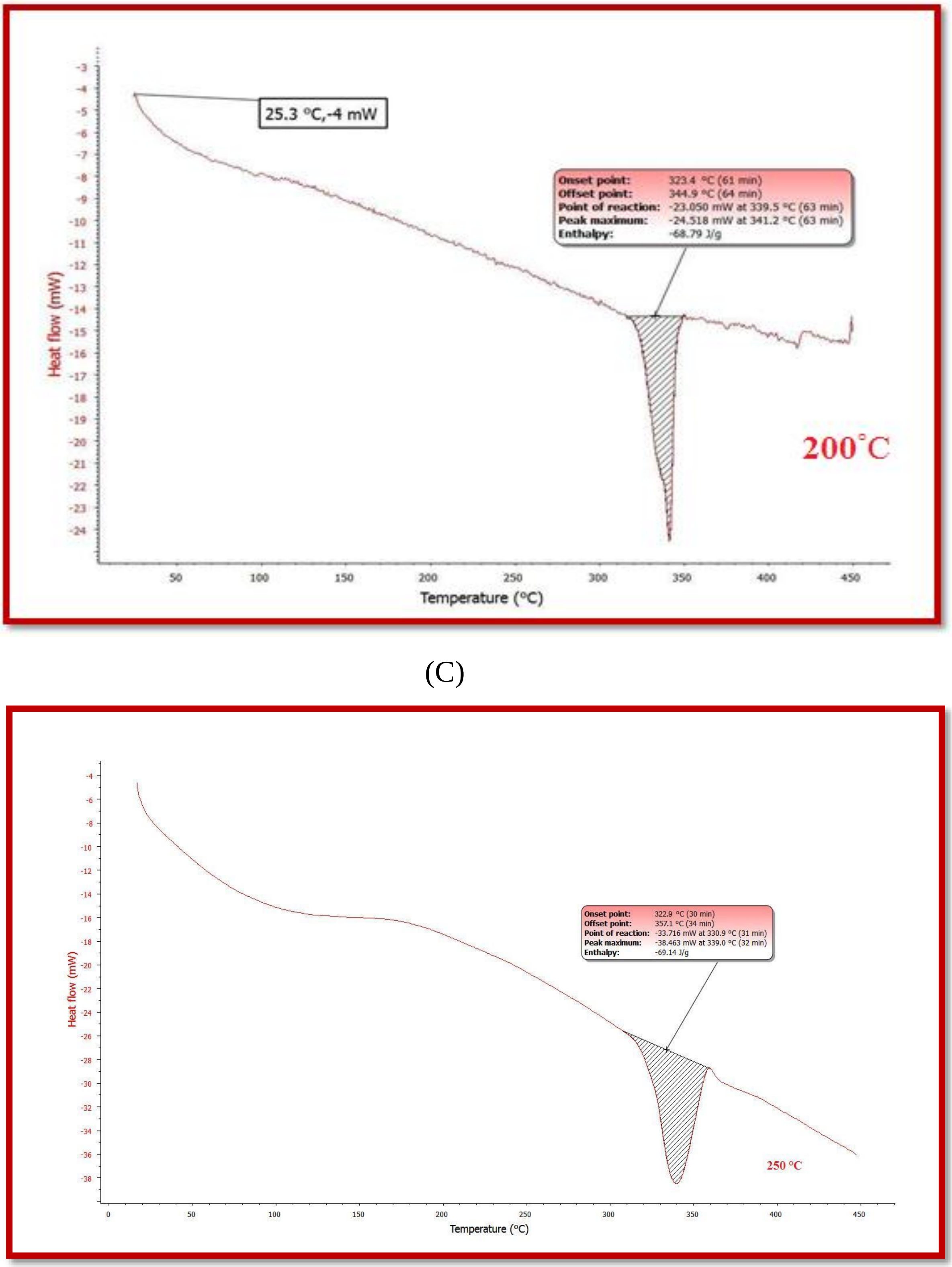
For type (1)


Heat flow (mW)
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
-15
-16
-17
-18
-19
-20
-21
-22
-23
-24
-25
23.9 °C,-4 mW
Onset point: 333.1 °C (31 min)
Offset point: 347.6 °C (32 min)
Point of reaction: -22.075 mW at 340.8 °C (31 min)
Peak maximum: -24.055 mW at 342.5 °C (32 min)
Enthalpy: 64.03 J/g
RT
0
50
100
150
200
250
300
350
400
450
500
Temperature (°C)

(A)


Heat flow (mW)
-4
-6
-8
-10
-12
-14
-16
-18
-20
-22
-24
-26
-28
-30
-32
-34
-36
-38
-40
-42
-44
Onset point: 334.2 °C (29 min)
Offset point: 348.8 °C (31 min)
Point of reaction: -42.222 mW at 341.7 °C (30 min)
Peak maximum: -44.749 mW at 343.4 °C (30 min)
Enthalpy: -65.50 J/g
100 °C
50
100
150
200
250
300
350
400
450
Temperature (°C)

(B)



(C)

(D)

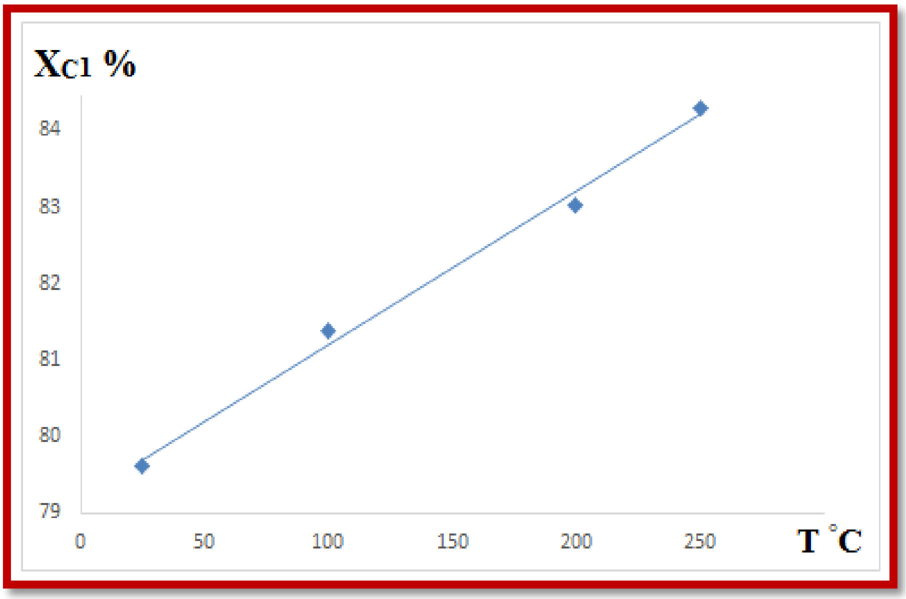
Fig. (4 -7) (A-D) the heat content function to temperature for type (2)

The peak endothermic in DSC curve shows the enthalpy of melting for poly (tetrafluoroethylene) samples during the initial "as received" heating by using equation (2-6) to calculate percentage of crystallinity based about (82 j/g) for the (100%) crystalline material. The reliance curve of temperature of changing enthalpy is found by integration of DSC curve almost accorded with diffraction intensity. In heating process the melting behavior of PTFE is concluded to create from increasing crystallinity and this is crystallization. The result for PTFE samples studied are given for both types in the table (4-4)

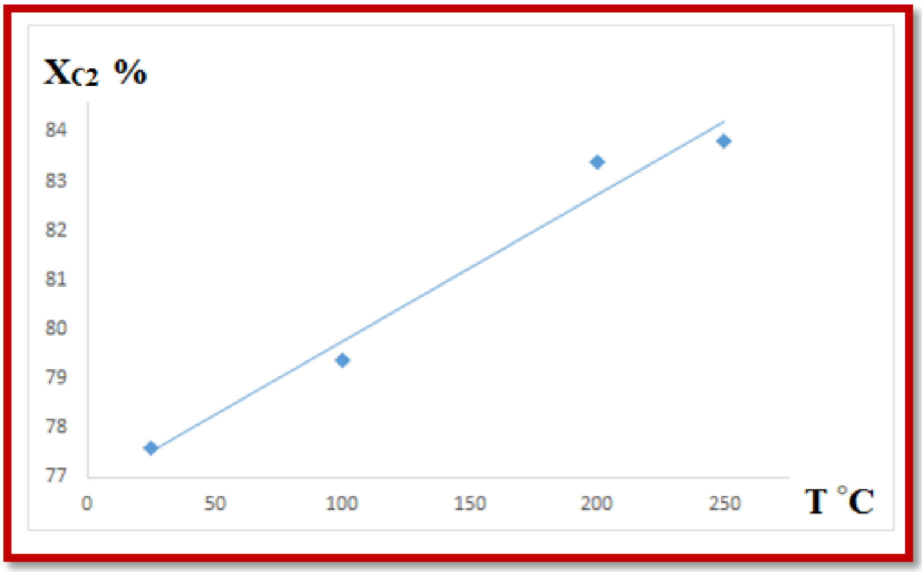
Table (4-4): DSC characterization of PTFE samples after heat treatment for both types

Type	T ˚C	Melt outset temperature (˚C)	peak maximum (°C)	Enthalpy j/g	X_C %
(1)	RT	320.3	339.5	65.69	79.62
	100	322.7	340	67.14	81.38
	200	324.7	338.7	68.51	83.04
	250	331.8	339.5	69.55	84.3
(2)	RT	333.1	342.2	64.03	77.612
	100	334.3	343.4	65.5	79.39
	200	323.4	341.2	68.79	83.38
	250	322.9	339	69.14	83.8

The results directly reflect that the increase of the degree of crystallinity of type (1) which is better than type (2) because of purely for type (1) which is better than type (2), the way of preparation and the elimination of previous processing thermal history effects which are reasonable to assume that all of these polymers would now have the same final characteristics. By subjecting polymer specimens to different "thermal treatments" in (DSC) prior to determining crystallization, more may be learned about optimal manufacturing conditions.



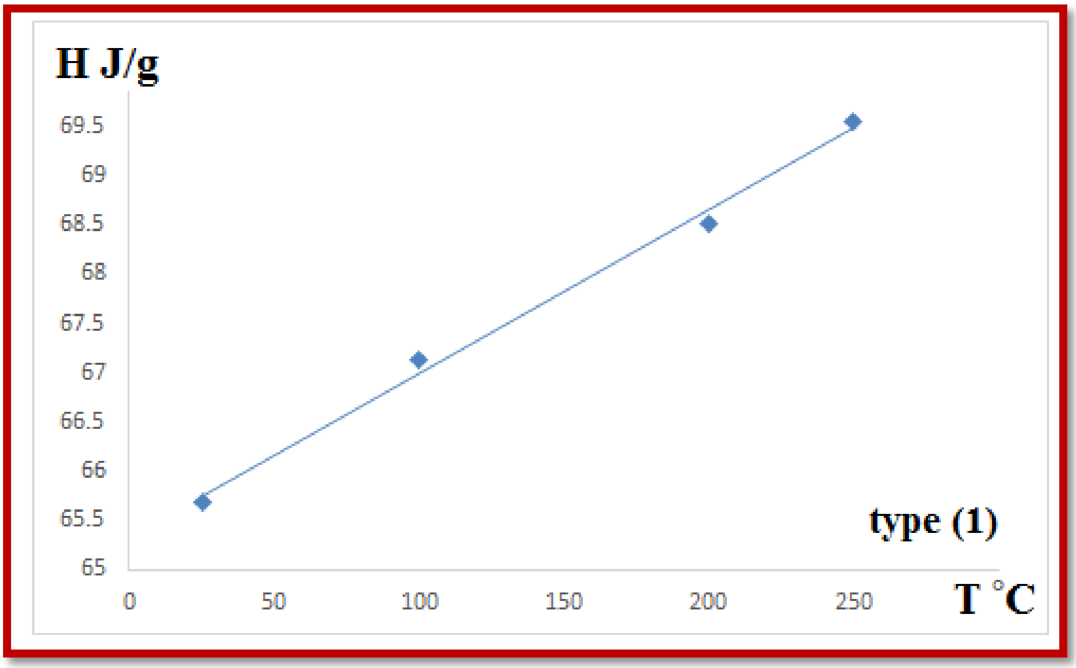
(a)



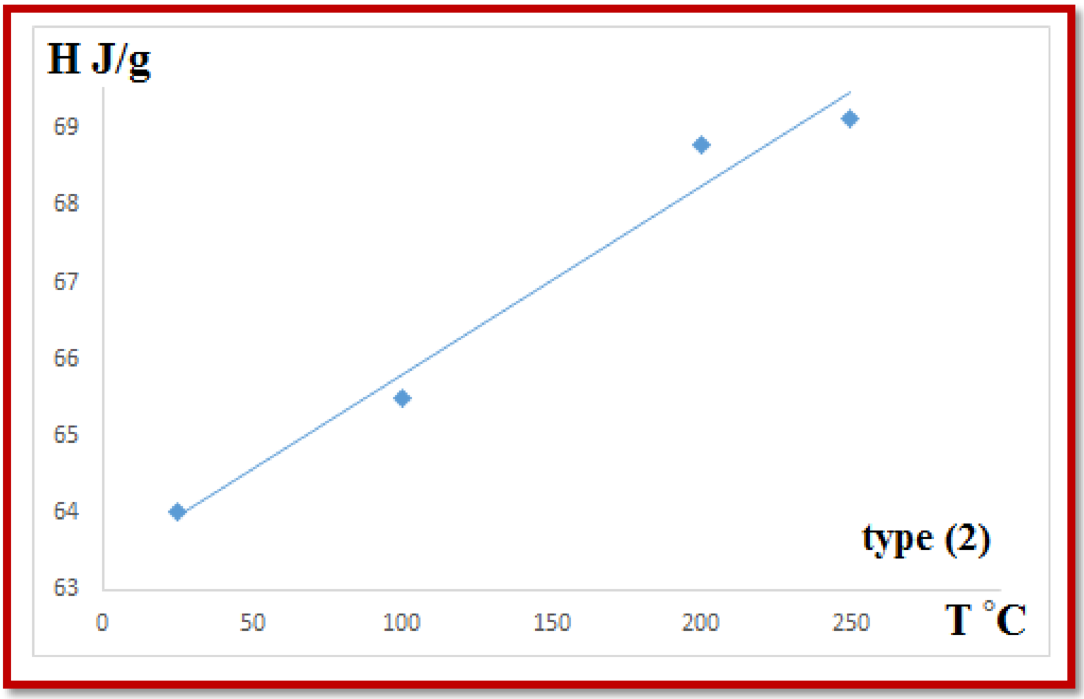
(b)

Figure (4-8) (a,b) show the increase of crystallinity with increasing temperature for two types

We can see the increasing enthalpy with increasing temperature like in figure (4-9)



(a)



(b)

Figure (4-9) (a,b) show the increasing Enthalpy with increasing temperature for two types.

(4-2) Shrinkage:

Shrinkage calculated for Poly (tetrafluoroethylene) samples that are free to shrink after heat treatment for type (1) and type (2) at different temperatures in figure (4-10) which shows the percentage of shrinkage as a function of temperature for both types.

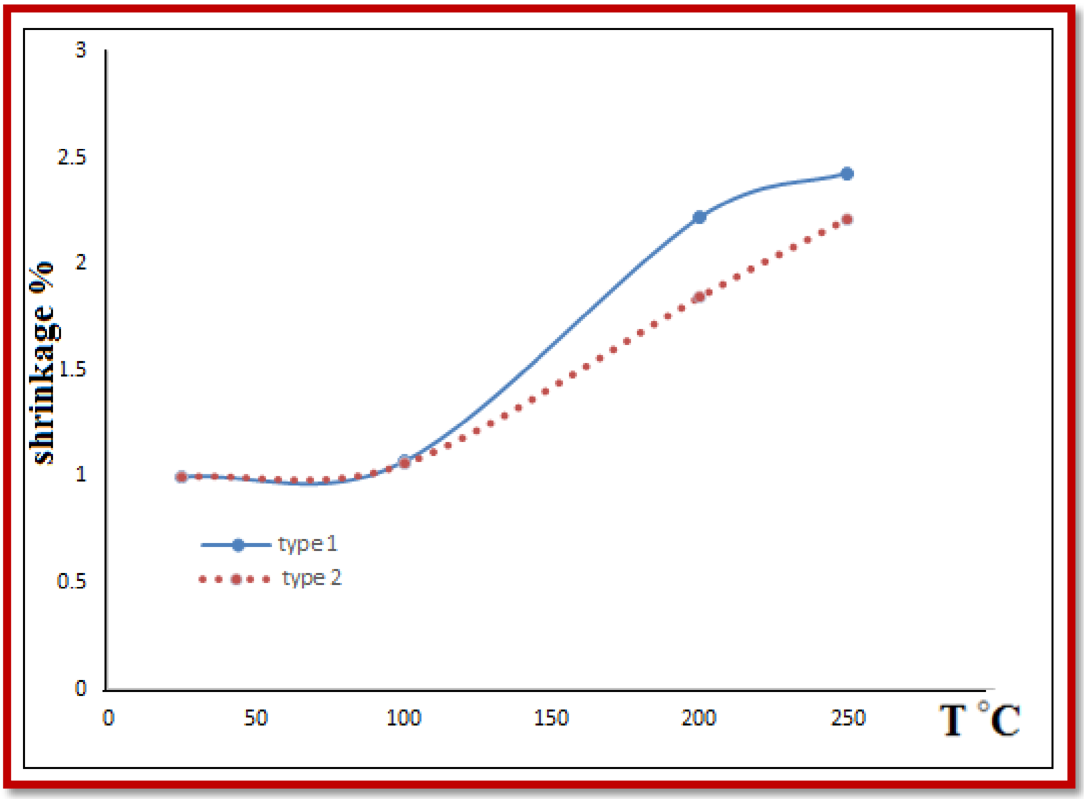


Figure (4-10) The percentage of shrinking with temperature for polymer PTFE

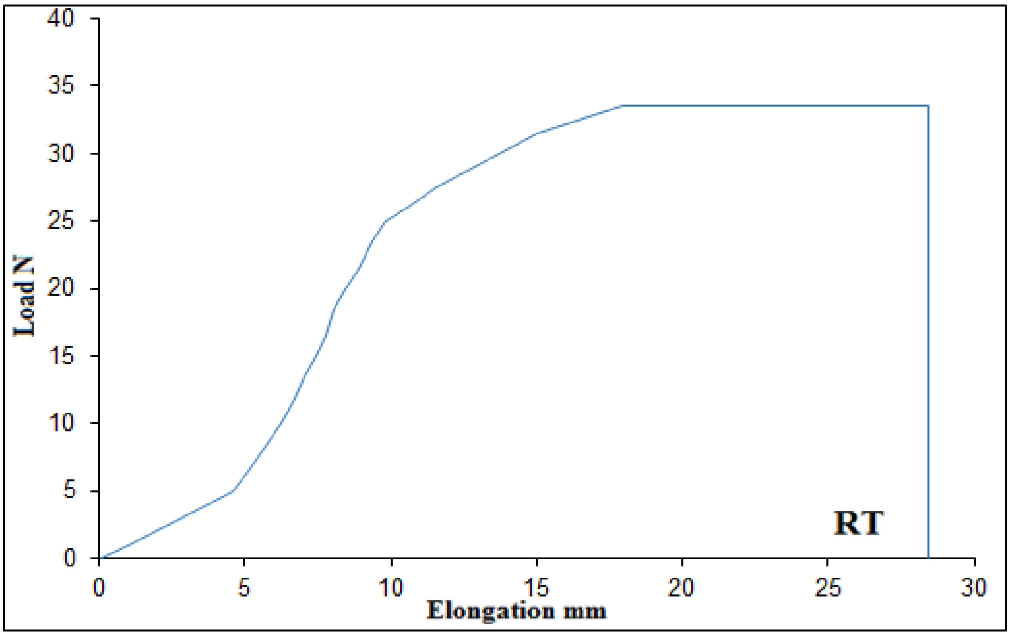
We can show the shrinkage of type (1) is higher than type (2) at the same temperatures because the way of preparing for samples, also we can show the shrinkage more increases when exceeds the glass temperature (T_g).

(4-2) Mechanical properties:

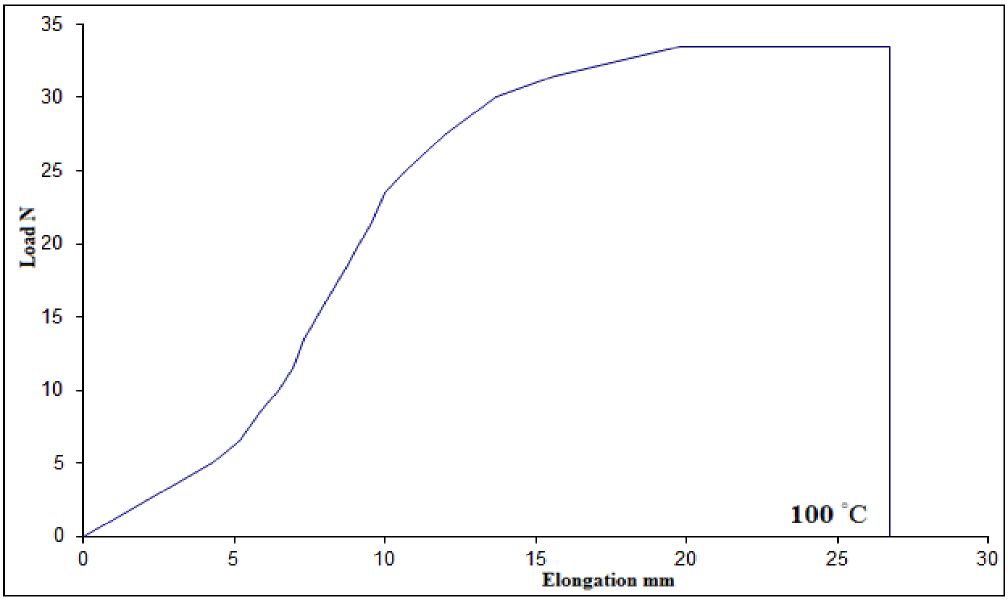
(4-2-1) Tensile test:

Load-Elongation curves for two types of PTFE samples are shown in figures (4-11) and (4-12) respectively.

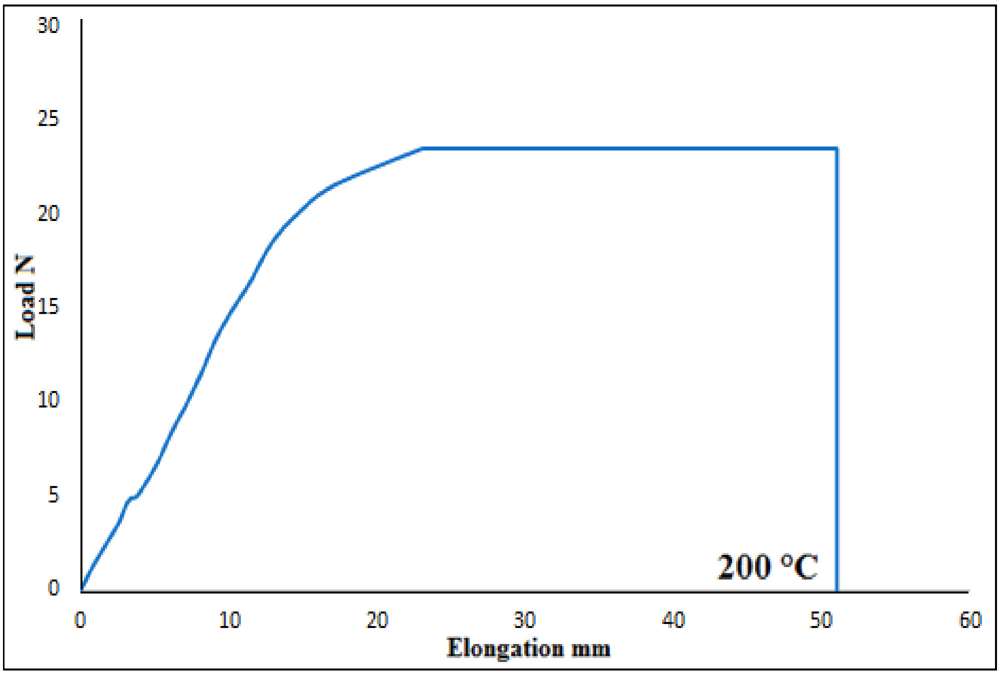
From these tensile curves for PTFE, we can get young's modulus, stress at break, stress at yield, elongation at yield. And elongation at break, which displayed in tables (4-5).



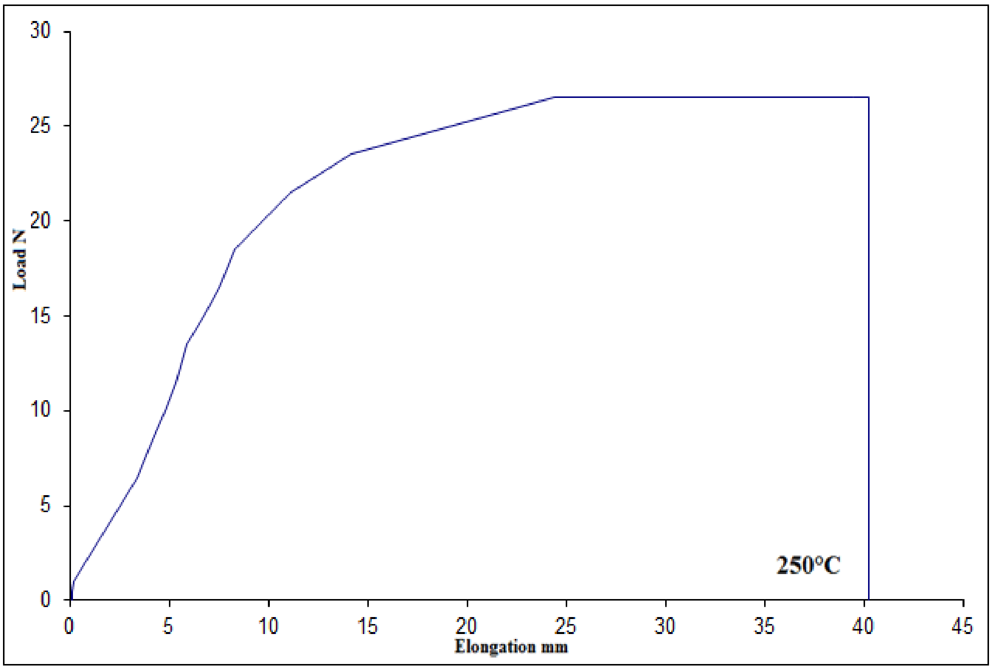
(A)



(B)

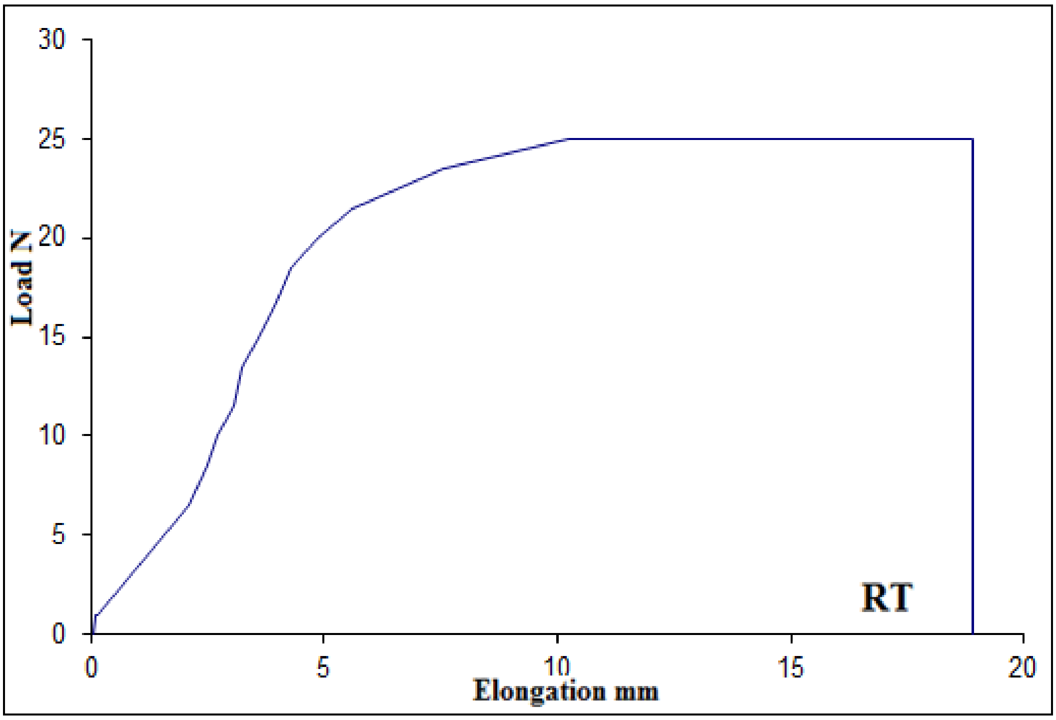


(C)

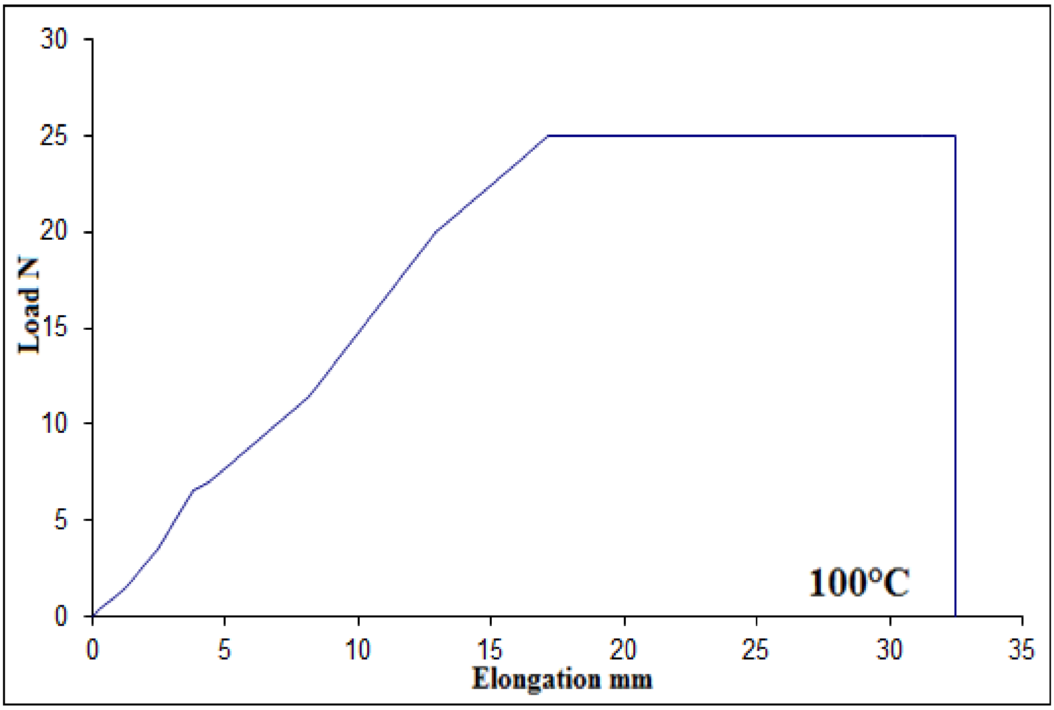


(D)

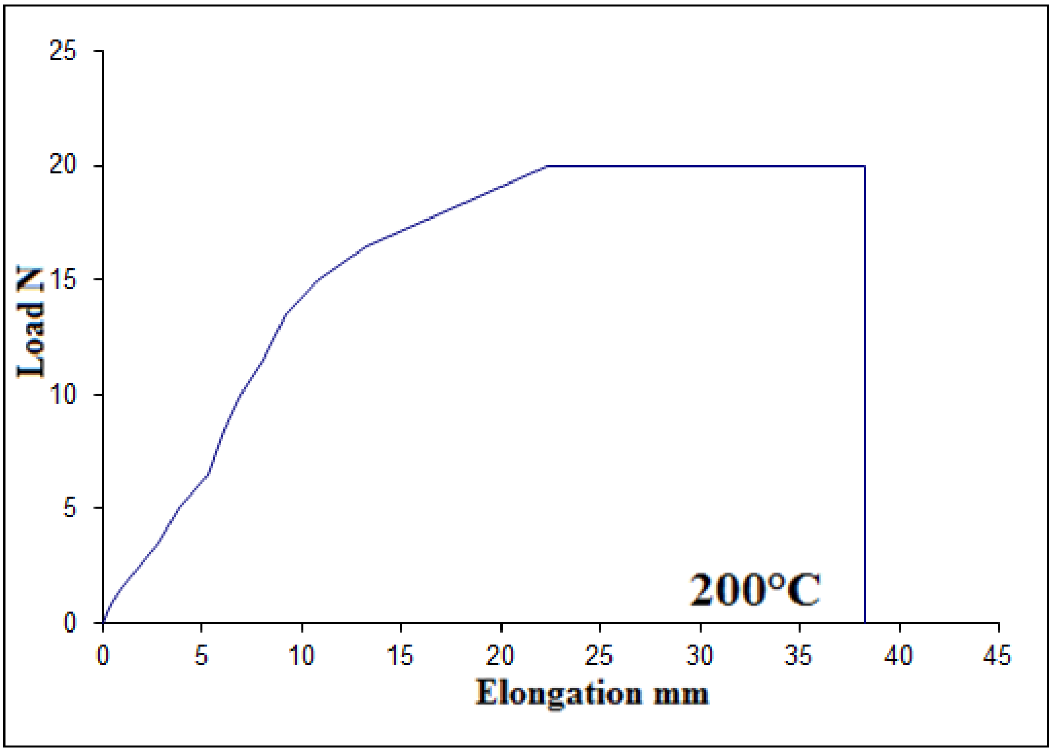
[Fig. (4-11) (A-D) Load-Elongation curve for PTFE (type 1)


Load N
30
25
20
15
10
5
0
0
5
10
15
20
Elongation mm
RT

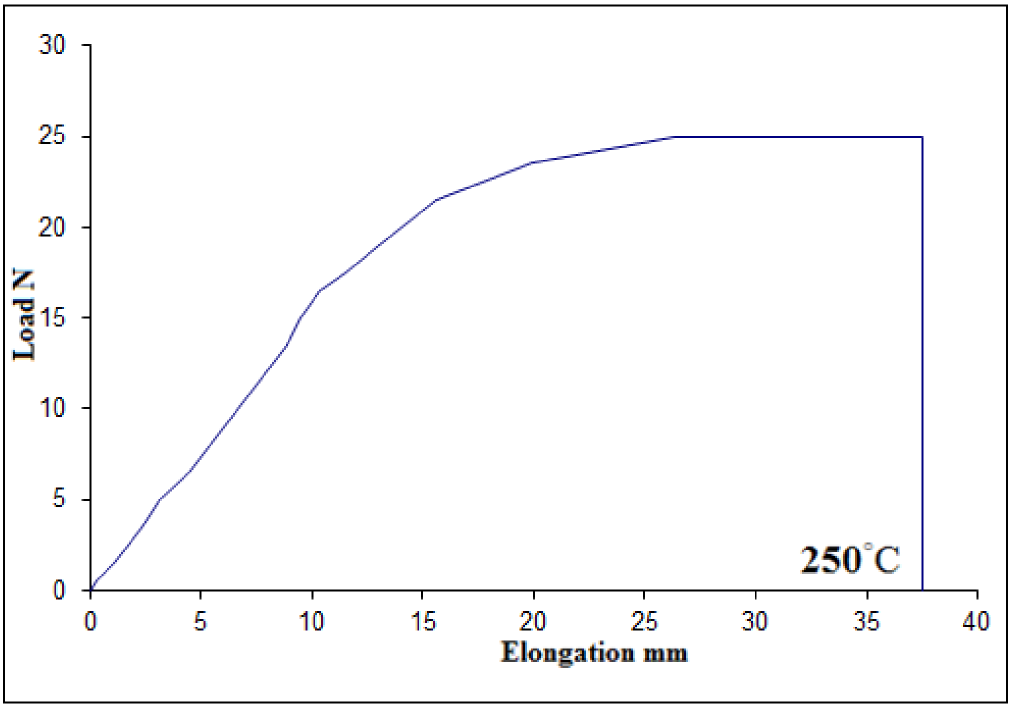
(A)


Load N
30
25
20
15
10
5
0
0
5
10
15
20
25
30
35
Elongation mm
100°C

(B)



(C)



(D)

Fig. (4-12) (A-D) Load-Elongation curve for PTFE (type 2)

By using equation (2-7) (2-8) and (2- 9) we calculated stress and strain for PTFE samples for all temperature.

Table: (4-5) tensile properties of PTFE for two types

Type	T (°C)	Y (Mpa)	σ_B (pa)	σ_y (pa)	ε_B (%)	ε_y (%)
(1)	RT	1.409	18190	16447	0.356	0.118
	100	1.142	22461	24896	0.421	0.21
	200	0.81	46735	29886	1.645	0.419
	250	1.094	47747	37837	2.056	0.5
(2)	RT	2.850	16447	13157	0.237	0.05
	100	2.203	20032	16025	0.515	0.203
	200	0.585	27159	22406	1.013	0.342
	250	0.827	41359	35566	1.209	0.5

From table (4-5) we can show the decrease in Young modulus with the increase of temperature because of the increase in stress with the increase in strain in type (1) slightly higher than type (2) Increased temperature leads to weakness the bonding strength between the molecular chains of the material and it occurs a great strain leading to the reduction of Young modulus this feature is applied for all semi-crystalline polymers.as in figure (4-13) below.

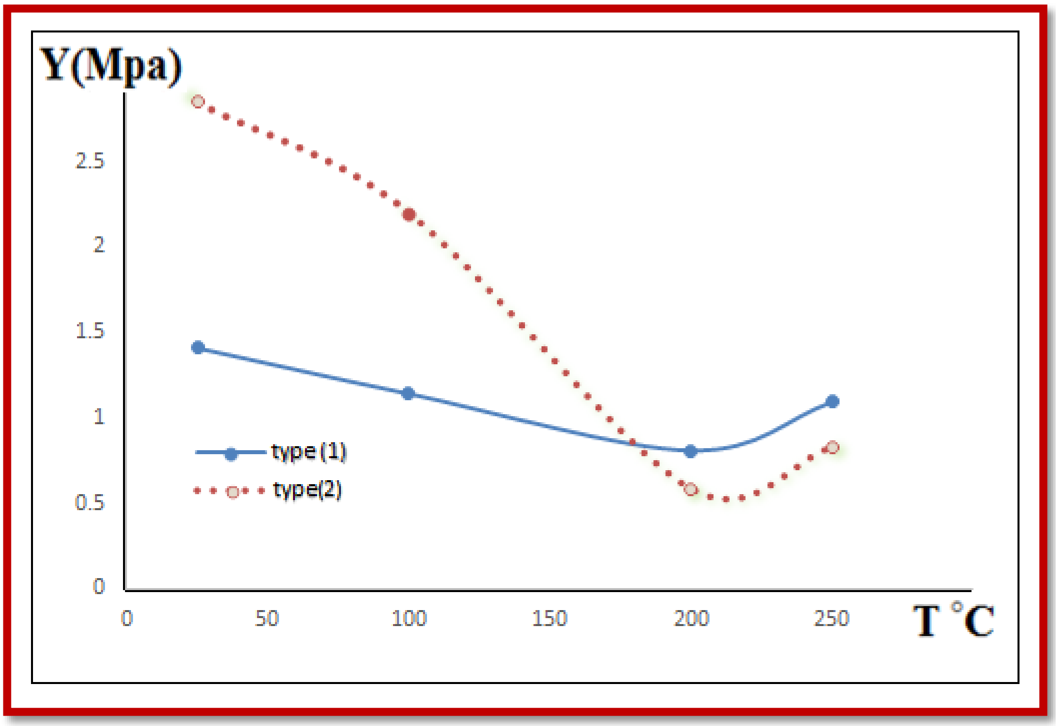


Figure (4-13) shows Young modulus as a function for heat treatment in different temperatures for two types of PTFE.

In another side the stress at break and stress at yield are increased with the increase of temperature and in type (1) which is higher than type (2) that is due to the increase of orientation of the molecular chains for polymer as in figure (4-14) and (4-15).

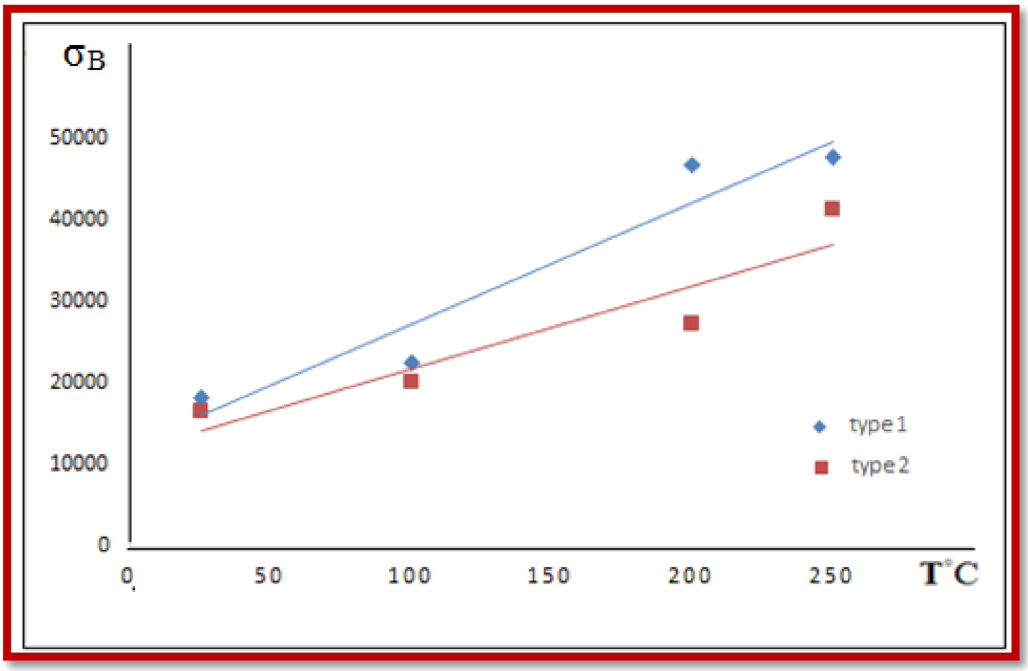


Figure (4 -14) shows stress at break as a function for heat treatment in different temperatures for two types of PTFE.

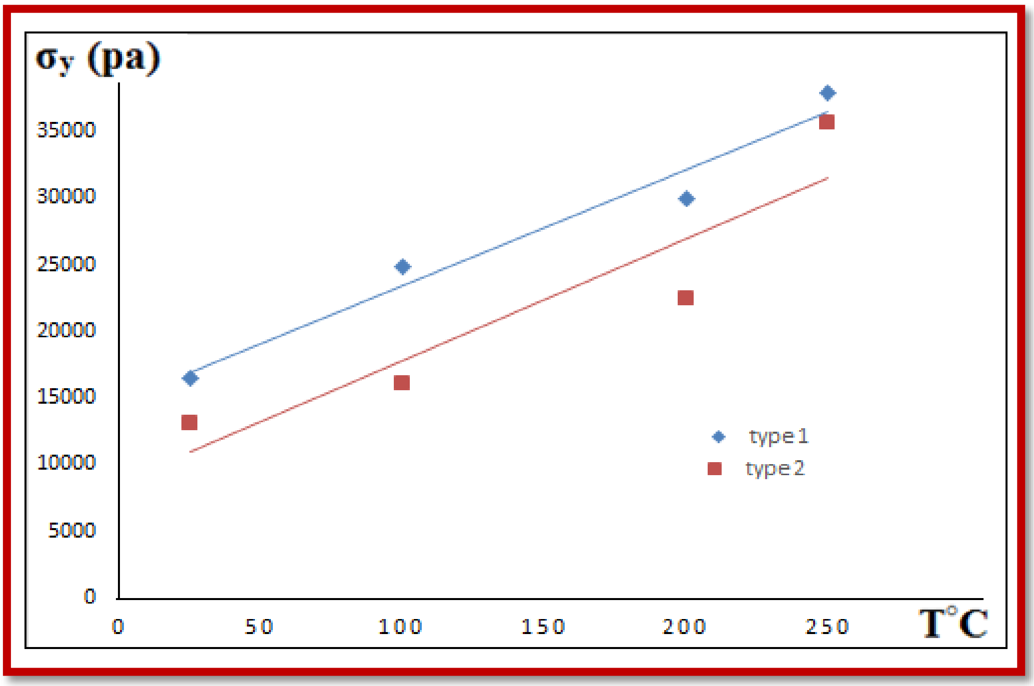


Figure (4-15) shows stress at yield point as a function for heat treatment in different temperatures for two types of PTFE.

Figure (4-16) and (4-17) show the behavior of strain at break and at yield for two types increase with the increase of temperature and in type (1) which is higher than type (2) this is due to making the samples free to shrinkage during heat treatment . The increase in the strain attributed to the flexible behavior of the polymer, which explains the carried strain of hanging on both crystalline and random areas with each other.

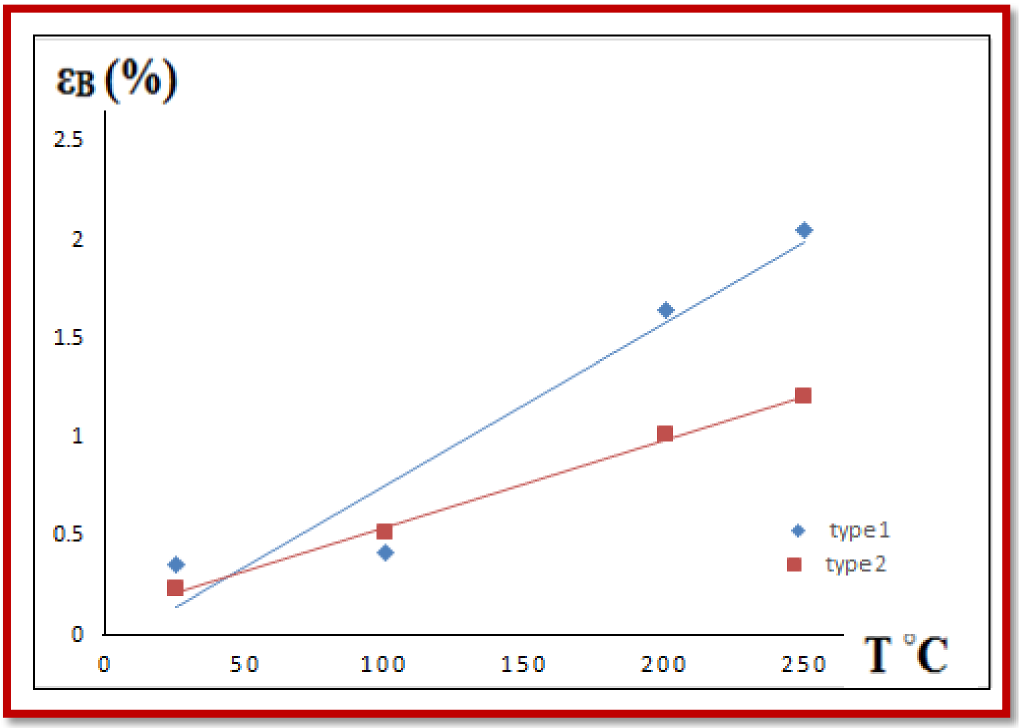


Figure (4-16) shows strain at breakdown as a function for heat treatment in different temperatures for two types of PTFE

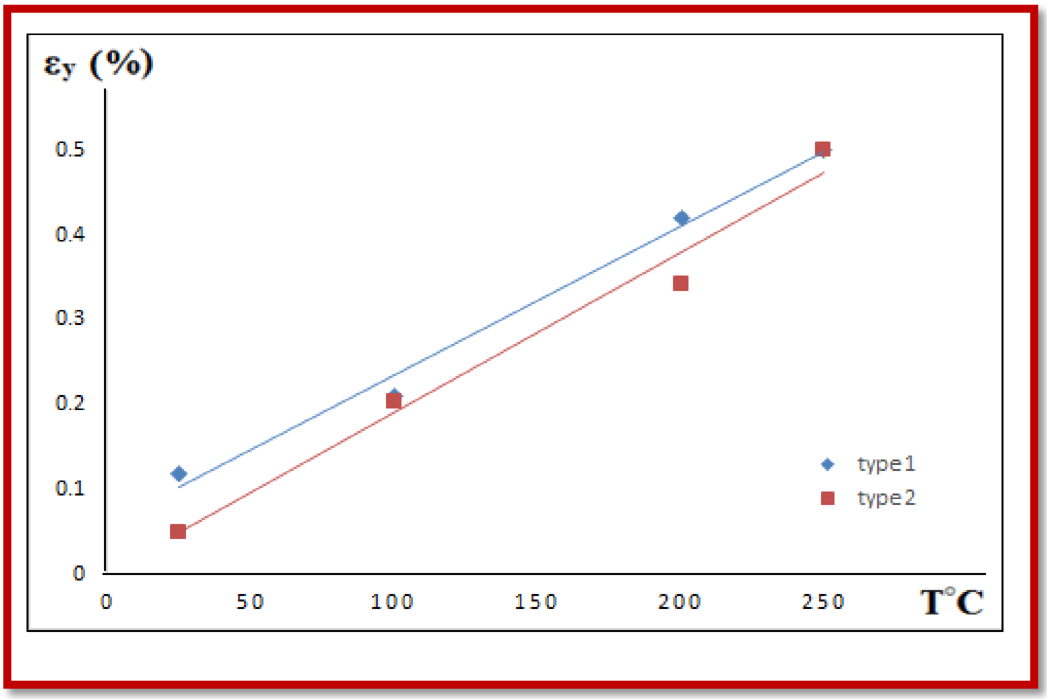


Figure (4-17) shows strain at yield point as a function for heat treatment in different temperatures for two types of PTFE

The heat treatment of polymer to different temperatures in order to know its properties and resistance to environmental conditions results showed that the mechanical properties increase linearly with the increase of temperature. The heat treatment led to improving the mechanical properties. Heating to (250°C) has led to the breaking of the bonds and formation of entanglement case which makes it the best and thus improving its properties for the appropriate environmental conditions.

Conclusions:

1- The heat treatment affected to the polymer PTFE for two types and improve the degree of crystallinity which will be increased with the increase of the heat treatment for both types, but the type (1) measured the degree of crystallinity better than other type. Because purity is further than the way of preparing this type, it affected on the results in both methods XRD and DSC.

2- The best method of measuring crystallinity is to construct the completely enthalpy diagram and compare it with reliable theoretical values such as what can be obtained from the ATHAS data base.

3- The thermal behavior for two types of polymer similar with some differences in the glass transition and melting point because of the nature of the sample and the way it is formed.

4- The enthalpy increases with the increase of temperature of two types of PTFE.

5- The decrease in Young modulus with the increase of temperature because of the increase in stress with the increase in strain and in type (1) which slightly higher than type (2) because the strain in type (2) is less than type (1)

6- The stress at break and stress at yield are increased with the increase of temperature and in type (1) which is higher than type (2) that is due to the increase in orientation molecular chains for polymer and the behavior of strain at break and at yield for two types which increase with the increase of temperature and in type (1) which is higher than type (2) that is due to make the samples free to shrinkage during heat treatment so the heat treatment led to improve the mechanical properties of PTFE.

Suggestion:

1- We can employ other polymeric materials and make the same measurements like:

-Polyethylene (PE)

-Polyethylene terephthalate (PET)

-Polybutylene terephthalate (PBT)

2- Exposing the polymer to other conditions such as beam.

3- Study another mechanical properties for PTFE.

Conclusions:

1- The heat treatment affected to the polymer PTFE for two types and improve the degree of crystallinity which will be increased with the increase of the heat treatment for both types, but the type (1) measured the degree of crystallinity better than other type. Because purity is further than the way of preparing this type, it affected on the results in both methods XRD and DSC.

2- The best method of measuring crystallinity is to construct the completely enthalpy diagram and compare it with reliable theoretical values such as what can be obtained from the ATHAS data base.

3- The thermal behavior for two types of polymer similar with some differences in the glass transition and melting point because of the nature of the sample and the way it is formed.

4- The enthalpy increases with the increase of temperature of two types of PTFE.

5- The decrease in Young modulus with the increase of temperature because of the increase in stress with the increase in strain and in type (1) which slightly higher than type (2) because the strain in type (2) is less than type (1)

6- The stress at break and stress at yield are increased with the increase of temperature and in type (1) which is higher than type (2) that is due to the increase in orientation molecular chains for polymer and the behavior of strain at break and at yield for two types which increase with the increase of temperature and in type (1) which is higher than type (2) that is due to make the samples free to shrinkage during heat treatment so the heat treatment led to improve the mechanical properties of PTFE.

References:

1- F. Belme "Basics of Polymers Science", ed. U.o. Mousel. College of Science (1971).

2- F.M. Ashby, R.W. Messler, R. Asthana, E.P. Furlani, R.E. Smallman, A.H. Ngan, J. Roy and N. Mills "Engineering Materials and Processes Desk Reference"1st edition, Butterworth-Heinemann, USA, (2009).

3- V.Raphanvan "Material Science& Engineering a first Course", 2nd, Prentice -Hall of India Private Limited, New Delhi, (1979).

4- V.K. Samarov, E. Bisikalov, A. Seliverstov and D. Seliverstov "HIP of Complex Shape Parts from Various Ti Alloys" International Conference on Hot Isostatic Pressing. Kobe, Japan, Vol.1, No.13, PP.1-6, (2011).

5- P.J. Raea and D.M. Dattelbaum "The properties of poly (tetrafluoroethylene) (PTFE) in compression", Polymer, Vol.45, No.22, PP.7615-7625, (2004).

6- B.D. Ratner, A.S. Hoffman, F.J. Schoen and J.E. Lemons "Biomaterials Science: An Introduction to Materials in Medicine", 2nd. London: Elsevier Academic Press, (2004).

7- B.K. Smith, C.D. Brown, G. LaVigne and J.J. Sniegowski " Thin Teflon-like films for MEMS: film properties and reliability studies" Micromachining and Microfabrication Process Technology IV USA, Vol. 3511, PP.114-124, (1998).

8- E.S. Clark" The molecular conformations of polytetrafluoroethylene", Polymer, USA, Vol.40, No.16, PP. 4659–4665, (1999).

9- D.M. Price and M. Jarratt "Thermal conductivity of PTFE and PTFE composites" Thermochimica Acta UK, Vol.392, PP.231-236, (2002).

10- Y. Qiu, Y. Gao, L. Wang and D. Zhang" Efficient light emitting diodes with Teflon buffer layer" Synthetic Metals, China, Vol.130, No.3, PP. 235–237, (2002).

11- , S. Okabe, M. Tanigaki, K.I. Kurumada, M. Ohshima and S.I. Kanazawa " Morphology change in polytetrafluoroethylene (PTFE) porous membrane caused by heat treatment" Polymer Engineering & Science, Vol.40, No.3, PP.817-809 , (2000).

12- L. Ylianttila and J. Schreder "Temperature effects of PTFE diffusers. in 9th International Conference on New Developments and Applications in Optical Radiometry", Optical materials, Vol.27, No.12, PP.1811-1814, (2005).

13- N.L. McCook, D.L. Burris, G.R. Bourne, J. Steffens, J.R. Hanrahan and W.G. Sawyer" Wear resistant solid lubricant coating made from PTFE and epoxy", tribology letters, Vol. 18, No. 1, PP.119-124, (2005).

14- Xu Chen and S. Hui "Ratcheting behavior of PTFE under cyclic compression" Polymer testing, China, Vol.24, No.7, PP.829–833, (2005).

15- C. Jing, J. Fengchun, S.V. Kenneth, A.M. Marc and F.N. Vitali "Mechanical and microstructural properties of PTFE/A1/W system" American Institute of Physics San Diego, USA, Vol.978, No.0, PP.723-726, (2007).

16- Y.A. Lebedev, Y.M. Korolev, V.M. Polikarpov, L.N. Ignat’eva and E.M. Antipov "X-ray powder diffraction study of polytetrafluoroethylene" crystallographic report, Russia, Vol. 55, No.4, PP.609-614, (2010).

17- N.S. Ali " Osmotic Distillation Process Using Polytetrafluoroethylene (PTFE) Microporous Layer Supported by a Polypropylene (PP) Net" Thesis, University of Technology, Iraq, (2009).

18- M. Yari and O. Moradi "Synthesis Polytetrafluoroethylene (PTFE) Nanoparticles via Adsorption of TFE Monomer onto Different Surfaces "Journal of nanostructury (Islamic Azad University) Iran, Vol 19, No. 12, PP.180-192, (2010).
T. Kitamura

19- Y.R. kharde and K.V. Saisrinadh " Effect of oil and oil with graphite on tribological properties of glass filled PTFE polymer composites" Bull mater science ,Vol. 34, No. 4, PP.1003–1012, (2011).

20- J. Blumm, A. Lindemann, M. Meyer and C. Strauser "Characterization of PTFE Using Advanced Thermal Analysis Techniques" International Journal of Thermophysics, springer US, Vol. 31, No.10, PP.1919-1927, (2010).

21- L. Nunes, F. Dias and H.S. da Costa Mattos "Mechanical behavior of polytetrafluoroethylene in tensile loading under different strain rates", Polymer Testing, Brazil, Vol.30, No.7, PP. 791–796, (2011).

22- R. Canto, N. Schmitt, J. Carvalho and R. Billardon "Experimental analysis to identify the deformation mechanism during sintering of cold compacted (PTFE) powder" polymer engineering and science, Vol.51, No.11, (2011).

23- G. Cihat, P. Zeynep and T. Vedat, 15th international research /Expert conference "Trends in the development of machinery and associated technology", Prague, Czech Republic, PP.12-18, (2011).

24- A. Atta and H.E. Ali "Structural and Thermal Properties of PTFE Films by Argon and Oxygen Plasma" Arab Journal of Nuclear Science and Applications Egypt, vol.46 No.5, PP.106-114, (2013).

25- K. MinJoong, J. GiSu, E. KwangSup, C. EunAe, R. JoungWook, K. Hyoung-Juhn and K. HyukSang "Effects of heat treatment time on electrochemical properties and electrode structure of polytetrafluoroethylene - bonded membrane electrode assemblies for polybenzimidazole-based high-temperature proton exchange membrane fuel cells" International Journal of Hydrogen Energy, Vol. 38, No. 28, PP. 12335–12342, (2013).

26- M. Dumitraş "DTA and DSC study on the effect of mechanical Dispersion on poly (tetrafluorethylene) properties", Acta chemical lasi Romania, Vol.22, No.2, PP.63-74, (2014).

27- C.E. Carraher and R.B. Seymour "Polymer Chemistry", Seventh edition, united States of America on acid-free paper, CRC Press and Taylor & Francis Group, (2008).

28- G. Odian "Principles of polymerization" Fourth Edition, Willey ,USA, (2004).

29- A. Kumar and R.K. Gupta "Fundamentals of polymer engineering", Second Edition, Marcel Dekker, Inc., USA, (2003).

30- J.R. Fried "Polymer science and technology", Third Edition, Pearson Education, USA, (2014).

31- J.V. Narlikar, "Chemistry PartΠ" National Council of Educational Research and Training, (2007).

32- S. Kalpakjian and S.R. Schmid, "Manufacturing Processes for Engineering Materials", fifth Edition, Pearson Education, Vol.12, (2008).

33- F. Kreith and S.A. Berger “Modern Manufacturing” Mechanical Engineering Handbook Ed Boca Raton: CRC Press LLC, Vol.10, (1999).

34- W. Michael, H. Bryce, B. Joseph, C. Michele, B. Uwe, B. Jeff, S. Tracy M.W. Jornitz, T.H. Meltzer and W.L. Gore "Expanded Polytetrafluoroethylene Membranes and Their Applications" Drugs and the Pharmaceutical Sciences, U.S.A.Vol.174, (2008).

35- S. Ebnesajjad 0T" Fluorplastics" Library of Congress, USA, (2000).

36- P. Fraundorf and S. Lin "Spiral powder overlays" Microscopy and Microanalysis, USA, Vol.10, No.502, PP.1356-1357, (2004).

37- A. Clearfield, J.H. Reibenspies and N. Bhuvanesh "Principles and Applications of Powder Diffraction" Wiley-Blackwel,

38- S. Kenny "Powder diffraction and the rietveld method" Lyngby, Denmark, (2008).

39- R. E. Dinnebier "Powder Diffraction "Theory and Practice, Germany, (2008).

40- R.J. Crawford, "Plastics Engineering", Third Edition, UK, St Edmundsbury Press Ltd, (2002).

41- R.O. Ebewele "Polymer science and technology" CRC Press, (2000).

42- T.R. Crompton "Polymer Reference Book" iSmithers Rapra PublishingUK, (2006).

43- J. Jia and D. Raabe "Crystallinity and Crystallographic Texture in Isotactic Polypropylene during Deformation and Heating" arXiv preprint, European Polymer Journal V.42,PP.1755-1766,(2006)

44- S. Jian-binsong, R. Min-qiao, C. Qing-yong, W. Shu-yun, Z. Qing-xiang, Z. Hong-fang and M. Zhi-shen " Determination of degree of crystallinity of nylon 1212by WAXD" Chinese journal of polymer science, vol.22, No.5, PP.491-496, (2004).

45- A. M. Hindeleh and R. Hosemann "polymer", Journal of Materials Science, vol.26, (1991).

46- M.A. Mohammed "Investigation of unit cell crystallinity and mechanical properties for polymer", Ph.D Dissertation university of Baghdad College of pure science Ibn-al haytham P.27, (2006).

47- S. M. Mulla, P.S. Phale and M.R. Saraf "Use of X-Ray Diffraction Technique for Polymer Characterization and Studying the Effect of Optical Accessories" ARAI, AdMet paper NOM Vol.6, (2012).

48- N.S. Murthy "Recent Developments In Polymer Characterization Using X-Ray Diffraction", The Rigaku Journal Japan, VOL. 18, NO. 1, PP.15-24, (2004).

49- M. Sobociński "Estimation of uhmpe crystallinity degree variation" Journal of Applied Mathematics and Computational Mechanics, Poland, USA, (2008). Vol.13, No.4, PP.117-122, (2014).

50- Y. Kong and J.N. Hay "The enthalpy of fusion and degree of crystallinity of Polymers as measured by DSC" European Polymer Journal UK, Vol.39, No.8, PP.1721-1727, (2003).

51- A.K. Bhargva and C.P. Sharma "Mechanical behavior and testing of materials" PHI learning, New Delhi, (2011).

52- D.R. Askeland and P.P. Phulé "The Science and Engineering of Materials" sixth edition, Cengage Learning, USA, (2010).

53- D.R. Askeland and W. Wright "Essentials of Materials Science and Engineering, 2nd Edition, Cengage Learning, Canada, (2014).

54- R.F. Landel and L.E. Nielsen "Mechanical properties of polymers and composites" 2nd Edition, CRC Press USA, (1993).

55- E. J. Hearn "Mechanics of Materials I", Third Edition, Butterworth-Heinemann, UK, (1997).

56- A.F. Liu "Mechanics and Mechanisms of Fracture: An Introduction", 1st Edition, USA, (2005).

57- B.S. Mitchell "An Introduction to Materials Engineering And Science", John Wiley & Sons, Inc. and Hoboken, New Jersey, Canada, (2004).

58- M.A. Meyers and K.K. Chawla "Mechanical Behavior of Materials", Cambridge University Press, UK, Vol. 2, PP.420-425, (2009).

59- W. Bolton, "Engineering science", Fifth edition, Routledge, (2006).

60- J. Margolis, "Engineering Plastics Handbook", McGraw-Hill, Canada, (2005).

61- W.D. Callister and D.G. Rethwisch "Fundamentals of Materials Science and Engineering", Fifth edition, John Wiley & Sons, Inc., USA, (2001).

62- S. Timoshenko, "Strength of Materials", second edition, D. Van Nostrand Company, USA, (1948).

63- F.Tieyuan, M. Zhishen, H. Ping, Q. Yuchen, W. Shuyun and C. Donglin "study of fraction affecting room temperature transition of PTFE" Chinese journal of polymer science, No.2, PP. 170-179, (1986).

64- M.A. Mohamed and N.N. Ramo "structural and mechanical different between met and UV stabilize poly amide 6, 6 subjected to heat treatment", College of Science of Al-Mustansiriya, Vol.24, N.1, P.127-134, (2013).

65- M. Yasuniwa, S. Tsubakihara, K. Ohoshit and S.I. Tokudome "X-ray studies on the double melting behavior of poly (butylene terephthalate) ", journal polymer science Vol. 39,No.17, PP.2005-2015, (2001).

66- J.W. Nicholson "The Chemistry of Polymers" 4 Edition, Royal Society of Chemistry, UK, (2012).

الخلاصة :

درس في هذا العمل نوعين من بولي تيترافلوروواثيلين (النقيين ولكن بأختلاف الشرك ة المصنعة PTFE) (صيني _اماراتي) بطريقه صب المحلول كأفلام رقيقه واشرطة ، بواسطه الخواص التركيبيه (حيود الاشعه السينيه ومسعريه المسح التفاضلي) والخصائص الميكانيكية بدلاله درجات حراره مختلفة للدوره الحرارية . يبين كلا النوعين تغير في الشده المستطاره من المستوى القاعدي (100) عند تغير درجه حرارة الدورة الحرارية واظهر النوعين زيادة في التبلورية مع زيا ة درجة الحرارة .كذلك اختلاف في الان ثالبي عند اختلاف درجات الحرارة حيث لوحظ زياة الانثالبي بزيادة درجة الحرارة واختلاف في الخصائص الميكانيكيه (الاجهاد والانفعال عند نقطة الخضوع ونقطه الكسر ومعامل يونك) للبوليمر حيث أظهرت المعالجة الحرارية للبوليمر بدرجات حرارة مختلفة من أجل معرفة خصائصه ومقاومته إلى الظروف البيئية ان الخواص الميكانيكية تزداد زيادة خطيا مع زيادة درجة الحرارة .

لوحظ بأن انتاج الشركه المصنعة الصينية أفضل من ناحية النتائج لأيجاد درجة التبلورية والخصائص الميكانيكيه عن انتاج الشركة المصنعة الأماراتية لنفس المادة البوليمرية.

جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة بغداد
كلية التربية للعلوم الصرفة /ابن الهيثم
قسم الفيزياء

دراسة تأثير المعاملة الحرارية على الخواص التركيبية والميكانيكية لبوليمر (بولي تيترافلورواثيلين)

رسالة مقدمة الى
مجلس كلية التربية للعلوم الصرفة / ابن الهيثم – جامعة بغداد
وهي جزء من متطلبات نيل درجة ماجستير علوم في الفيزياء
من قبل

رند باسم لطفي الكرخي

بكالوريوس علوم فيزياء / 2011
باشراف

د. مي عبد الستار محمد نجيب

1437هـ 2015 م