Structural properties between two types of PTFE subjected to heat treatment.

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Abstract

In this study two type of pure polytetrafluoroethylene (PTFE) (C_2F_4). China_UAE source prepared from solution cast as film and strip have been studied by structural properties (X-ray diffraction (XRD) and Differential Scanning Calorimetry (DSC).subjected to different temperature heating cycle. Both modifications show variation in the scattered X-ray intensity of the basal plane (100) as the temperature of heating cycle is changed .Moreover, the Enthalpy of each kinds is changed with difference of heat treatment .It seems that the product company of china is better than the product company of UAE in degree of crystallinity for this polymer .

Keywords: PTFE, degree of crystallinity, DSC

اختلاف الخصائص التركيبية لنوعين من بوليمر (بولي تيترافلورواثييلين PTFE) باختلاف درجات الحرارة .

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الخلاصة :

درس في هذا العمل نوعين من التفلون (PTFE) النقيين ولكن بأختلاف الشركة المصنعة (صيني _اماراتي) بطريقة صب المحلول كأفلام رقيقة واشرطة ، بواسطه الخواص التركيبية (حيود الاشعه السينية ومسعرية المسح التفاضلي) بدلاله درجات حرارة مختلفة للدورة الحرارية . يبين كلا النوعين تغير في الشدة المستطارة من المستوى القاعدي (١٠٠) عند تغير درجه حرارة الدورة الحرارية كذلك اختلاف في الانثالبي عند اختلاف درجات الحرارة و لوحظ بأن انتاج الشركه المصنعة الصينية أفضل من ناحية النتأئج لأيجاد درجة التبلورية عن انتاج الشركة المصنعة الأماراتية لنفس المادة البوليمرية .

الكلمات المفتاحية : بولي تيترافلورواثيلين ، درجة التبلورية ، مسعريه المسح التفاضلي .

Introduction:

The polymer described in this study is poly (tetrafluoroethylene) (PTFE). It chosen for several reasons including its use as a common engineering material for small high-performance parts and its availability from several manufacturers. While studied extensively in the past, it has received little attention in the open literature for the last 25 years. We have chosen to revisit this material because of its structural complexity PTFE is a remarkable material in many ways. It exhibits useful properties over the widest temperature range of any polymer. PTFE is better known by trade name Teflon. PTFE has a good chemical resistance, it is light-and weather-resistance and has no absorption of water .These properties make PTFE an attractive material for outdoor use [1]. The chemical structure of repeat unit of poly (tetrafluoroethylene) PTFE is presented in figure (1).

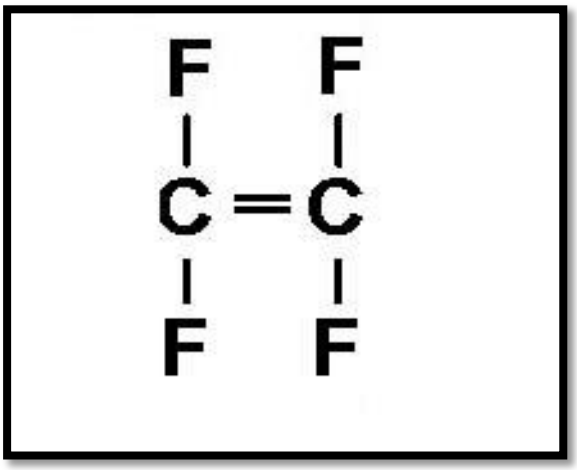


Figure (1) Repeat unit of poly (tetrafluoroethylene) (PTFE)

An understanding of the degree of crystallinity for a polymer is important since crystallinity affects physical properties such as storage modulus, permeability, density, and melting point. While most of these manifestations of crystallinity can be measured, a direct measure of degree of crystallinity provides a fundamental property from which these other physical properties can be predicted [2].

X-ray diffraction is a technique that measure intensity into or out of material as a function of Bragg's angle .This intensity is reported as percent crystallinity by normalizing the observed intensity to that of sample 100% crystalline for the same polymer [3].

Differential scanning calorimetry (DSC) is a technique which measures heat flow into or out of a material as a function of time or temperature. Polymer crystallinity can be determined with DSC by quantifying the heat associated with melting (fusion) of the polymer. This heat is reported as %

crystallinity by ratioing against the heat of fusion for a 100% crystalline sample of the same material, or more commonly by ratioing against a polymer of known crystallinity to obtain relative values. [4]

Experimental:

We used two sets samples of PTFE ribbon with different origins, the first set is a ribbon of polymer (PTFE) China origin and the second set is also a ribbon of (PTFE) but Emirates origin. By taking the bar is made of this article polymeric that 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.

X-ray diffraction scans were performed on (Shimadzu 6000) diffractometer fitted with monochromatic CuK_{α} radiation at a scam speed of (0.02 $deg.sec^{1}$)and θ angle between 10 to70 degrees.

Four X-ray different temperature patterns measured for each samples in different temperatures (RT, 100,200,250) $^{\circ}C$ to determine the average integrated intensity of the reflection (100).

To estimate the degree of crystallinity for PTFE we determined the peak by integrating the corresponding area in the X- ray patterns .First we found the total area of the crystalline and amorphous components (after the subtraction of non-coherent scattering. Then the integrated intensity of the peaks of the crystalline phase were measured .The area of the amorphous hole was determined as the difference between the total and crystalline components.

The integrated intensity of the reflection at the θ angle of (18.05) was taken as the crystalline component of PTFE, because peaks of large angles make an in significant contribution to the scattering pattern.

A quantitative X-ray powder diffraction analysis was carried out of Hermans weidinger method [5] [6].

An X- ray diffraction scan in a plot of scattered X- ray intensity versus scattering angle. A diffraction scan of a crystalline polymer shows Bragg crystalline reflection and amorphous peak on it.

Let I_c and I_a be the area under certain selected crystalline peaks and amorphous peaks respectively, after correcting the intensity for in coherent scattering several X-ray apparent degree of crystalline have been defined follows [7] [8].

$$X_C = \frac{Ic}{Ic+Ia} \quad \text{.....(1)}$$

$$X_{C=} \; 1 + \frac{Ic}{Ia} \quad \text{.....(2)}$$

$$X_C = 1+(\frac{Ia}{Ic})^{-1} \ldots\ldots. (3)$$

The reason these are apparent rather than rigorous degree of crystallinity will be seen later when the basis of Roland's method is discussed.
Differential scanning calorimetry (DSC) were performed on DSC (STA.PT.1000.plant) by company (LINSEIS) Germany. The sample contained in a metal pan and the reference (usually an empty pan) sit on raised platforms on the cell's thermoplastic disk. As heat is transferred through the disk, the differential heat flow to the sample and reference is monitored by area thermocouples. A sample thermocouple directly monitors sample temperature. A preheated purge gas present to provide additional baseline stability as well as the desired sample-atmosphere interaction [9].

In this study, four samples of poly (tetrafluoroethylene) (PTFE) (RT, 100,200,250) °C

Were analyzed over the temperature range ambient to 400 °C .The programmed heating rate was 10 °C/min ;the atmosphere around the sample was nitrogen, since the previous thermal history of a polymer affects the measured degree of crystallinity by the relation :

$$X_c\% = \frac{\Delta H}{\Delta H^\circ} * 100\ \% \ldots\ldots (4)$$

Where ΔH is the enthalpy of the sample and ΔH° is the enthalpy of the totally crystalline to the same sample. These sample were evaluated both "as received" and after being subjected to a "thermal treatment" designed to impart equivalent thermal history to all four samples for each types [10].

Results:

XRD wide angle x-ray diffraction (WAXRD) 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 (2a) and (2b) for two type of PTFE specimens respectively. Four distinct peaks are observed in the spectra; the interplner spacing equation for triclinic system [11]. As shown in table (1)

Table (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	4.83	2.830	(110)
36.57	2.43	2.423	(200)
49	2.18	2.182	(210)

We were chose the intensity of the (100) plane because higher value of intensity than the other peaks .the intensity (100) increased in the type (1) better than in type (2) with increasing the heat treatment temperature up to 250 °C .This is due to possible re-orientation in the molecular chains caused by the heating cycle . In another side the way of preparation of those two types and the historical production of them effect on the orientation of the molecular chains, while the heating cycle is increased the order of orientation chains in type (1) better than type (2) that's mean the degree of crystallinity in type (1) is better than type (2) because of the way of preparation of these types with increasing the heating cycle .The degree of crystallinity calculated from equation (3) are given in table (2).

Table (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	٨٣,٥
	١٨,٠٤٧٦	١٠٠	٨٦,٥٤
	١٨,١٤٧٨	٢٠٠	٨٨,٦٣
	١٨,١٨٩٢	٢٥٠	٨٩,٤٤
(2)	١٨,١٣٤٤	RT	٧٥,٠٣
	١٨,١٤٠٣	١٠٠	٧٧,٨٤
	١٨,١٣٤٩	٢٠٠	٨٧,٢٩
	١٨,١٣١٤	٢٥٠	٨٩,١٣

It is notes that type (1) is more purely than type (2) which is given a good value for degree of crystallinity than another.

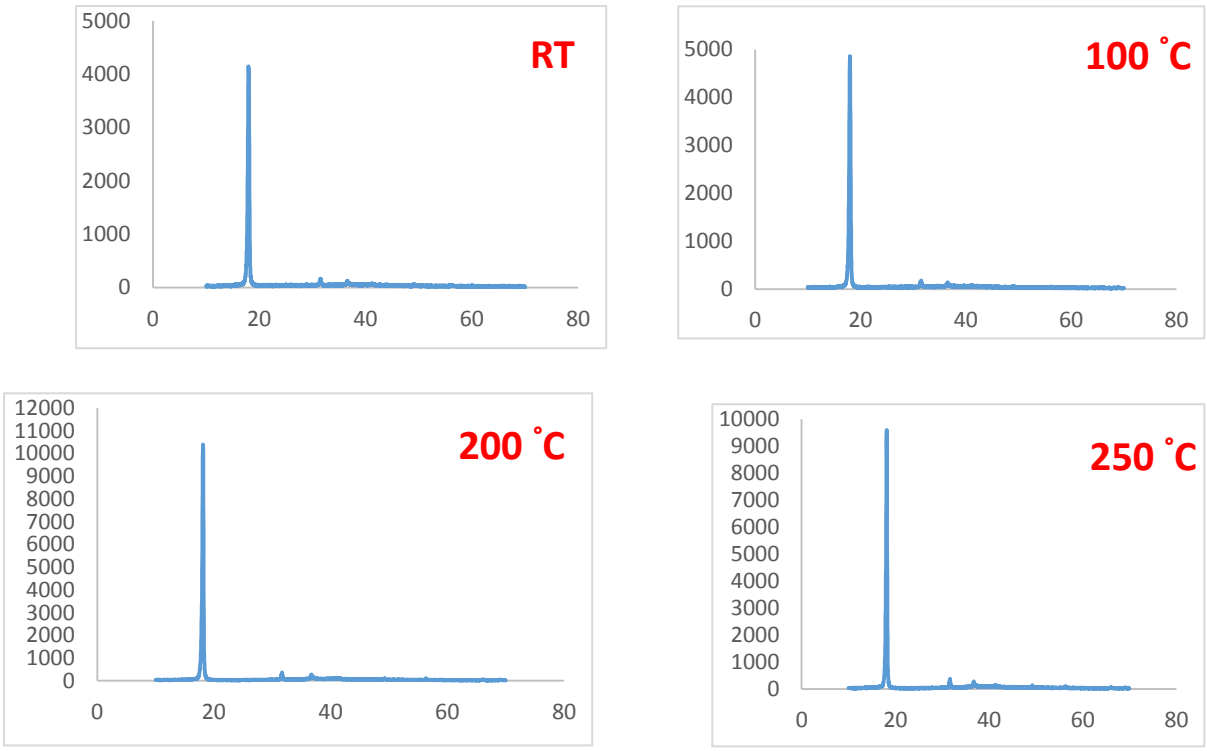


Figure (2-a) show the degree of crystallinity for type (1) with different temperature for polymer poly (tetrafluoroethylene) PTFE.

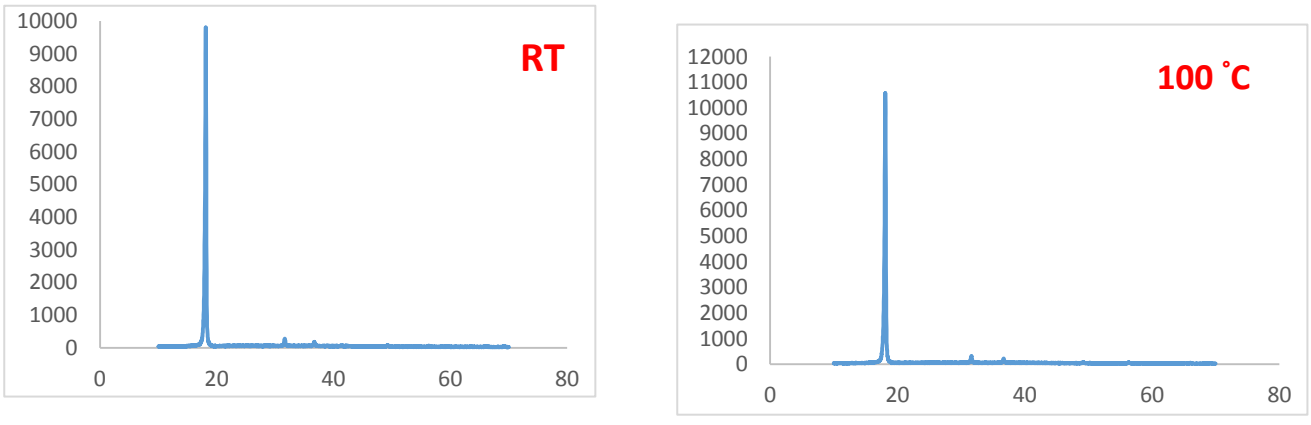
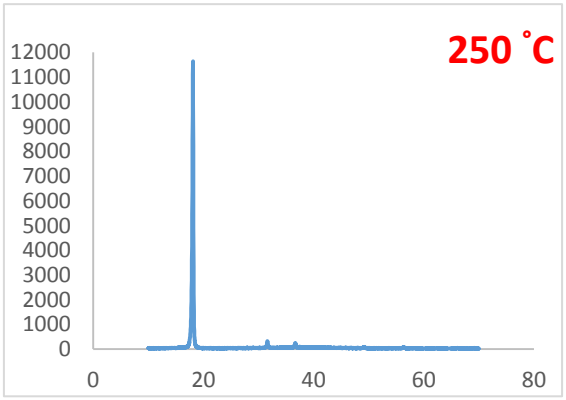
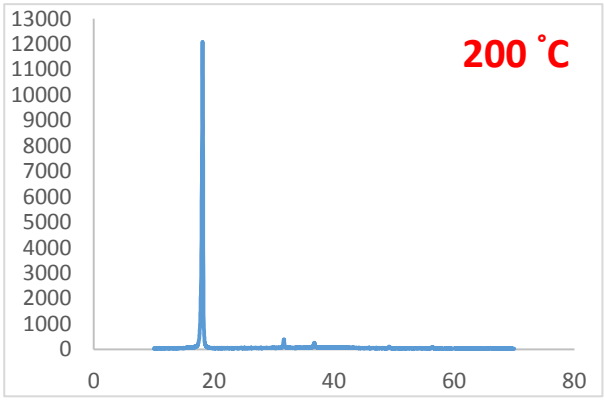


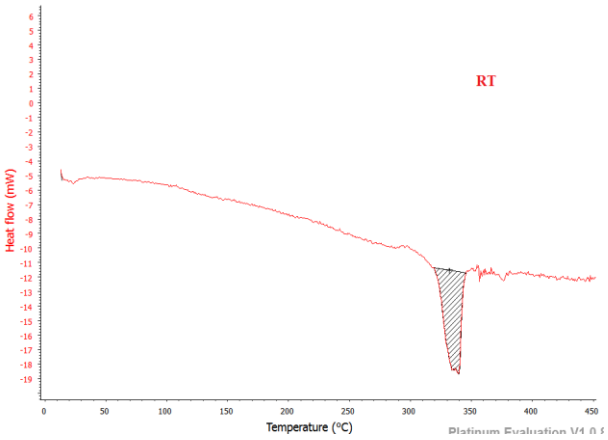
Figure (2-b) show the degree of crystallinity for type (2) with different temperature for polymer poly (tetrafluoroethylene) PTFE.

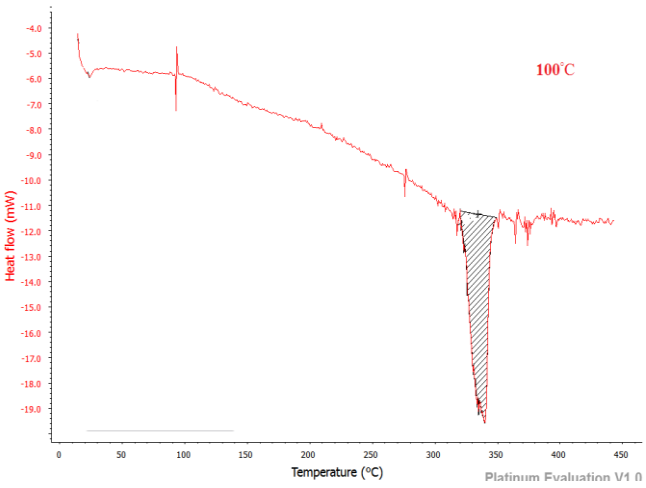




DSC

Figure (3-a) and (3-b) shows the melting endotherm for one of the of poly (tetrafluoroethylene) samples during the initial "as received" heating .By using equation (4) to calculate percent crystallinity based upon (82) j/g for the 100 % crystalline material [12].The result for the four samples studied are summarized for both types in table (3)





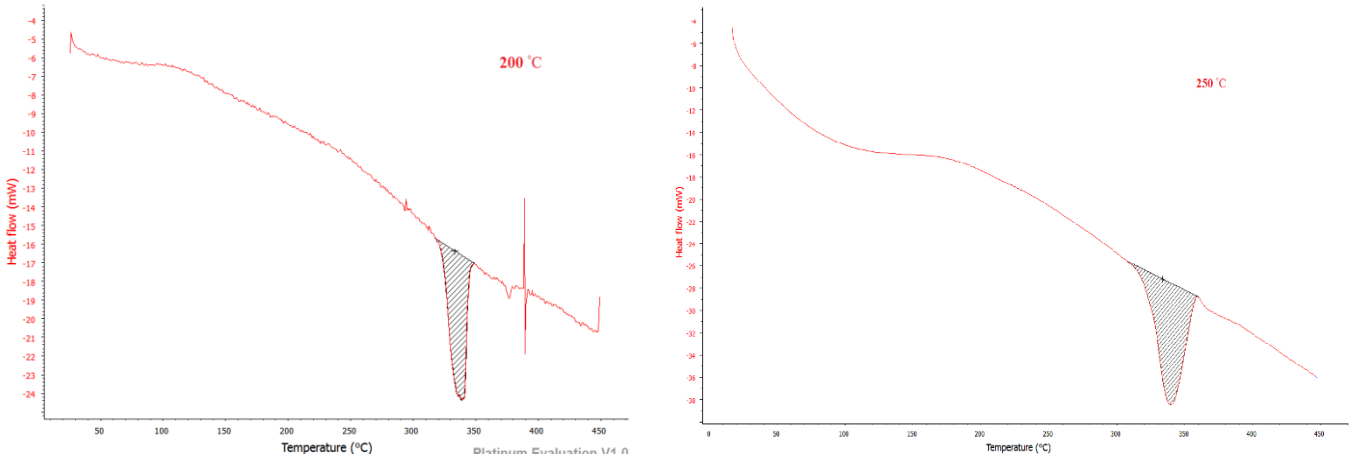


Figure (3a) the melting endotherm for one of the of poly (tetrafluoroethylene) by DSC

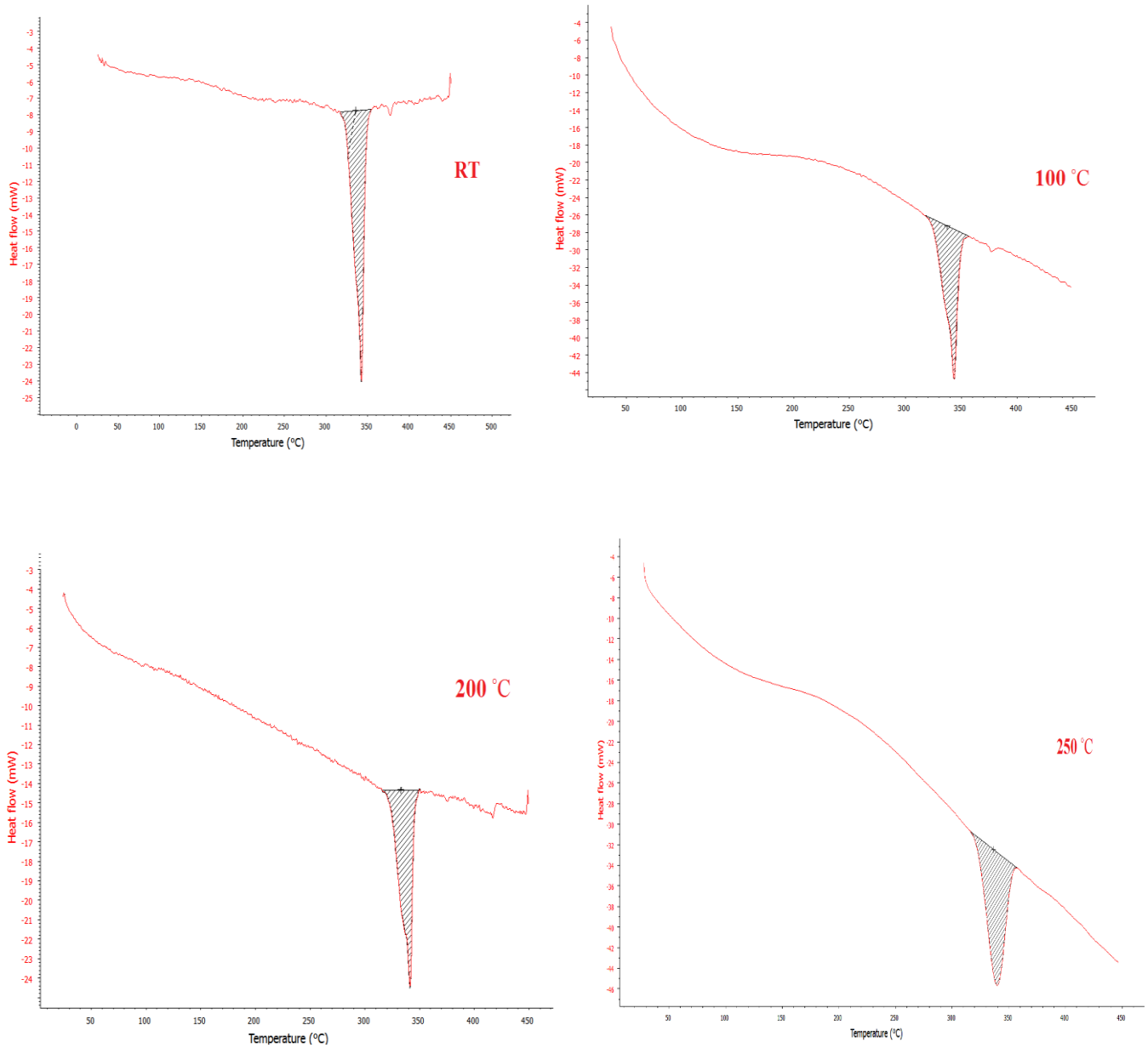


Figure (3b) the melting endotherm for one of the of poly (tetrafluoroethylene) by DSC

Table (3): DSC characterization of PTFE samples after heat treatment for both types

Type	T °C	Melt outset temperature (°C)	peak maximum (°C)	Enthalpy j/g	XC %
(1)	RT	320.3	٣٣٩,٥	٦٥,٦٩	٧٩,٦٢
	100	٣٢٢,٧	٣٤٠	٦٧,١٤	٨١,٣٨
	٢٠٠	٣٢٤,٧	٣٣٨,٧	٦٨,٥١	٨٣,٠٤
	٢٥٠	٣٣١,٨	٣٣٩,٥	٦٨,٥٥	٨٤,٣
(2)	RT	٣٣٣,١	٣٤٢,٢	٦٤,٠٣	٧٧,٦١٢
	١٠٠	٣٣٤,٣	٣٤٣,٤	٦٥,٥	٧٩,٣٩
	٢٠٠	٣٢٣,٤	٣٤١,٢	٦٨,٧٩	٨٣,٣٨
	٢٥٠	٣٢٢,٩	٣٣٩	٦٩,١٤	٨٣,٨

The results reflect directly increase of degree of crystallinity of type (1) better than type (2) because of purely for type (1) is better than type (2), the way of preparation and the elimination of earlier processing thermal history effects which are reasonable to assume that all of these polymers would now have similar final properties .By subjecting polymer samples to different "thermal treatment" in DSC prior to the crystallinity determination ,much may be learned about optimizing processing conditions.

Conclusions:

The degree of crystallinity will be increase with increasing the heat treatment for both types, but the type (1) measured the degree of crystallinity better than another type.

In general, for a pure polymer the best method of measuring crystallinity is to construct the completely enthalpy diagram and compare it with reliable theoretical values such as can be obtained from the ATHAS data base .However, most real world sample are not pure polymer they will be plastic or blended or contain fillers and another additives .this makes the enthalpy diagram approach un realistic in many cases, Then type (1) made from Company of China is pure than the type which made from a Company of UAE .

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