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Study the Effect of Temperature on Structural, Mechanical and Thermal Properties of PVC/$CaCO_3$ Composite

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Abstract:

In the present study, the structural properties which included the X-rays diffraction, and DSC, the mechanical properties, which include tensile test, three-point bending test (Bending Test), hardness test and thermal conductivity of the polymers reinforced with calcite (PVC/$CaCO_3$) at different temperature (25-40-80-120-160-200-220) °C. The research results showed that the X_C degree of X-ray diffraction decreased at high temperatures (220 ˚C), while the inter-polymerized polymer (PVC / $CaCO_3$) increased at high temperatures. The DSC test results showed that the degree of crystallinity (X_C) decreases at high temperatures (220 ˚C). The mechanical test results, their values were found to decrease at (220 ˚C) higher temperatures. Finally, the obtained results were indicated that the thermal conductivity values decrease at (220 ˚C).

Keywords: PVC, Structural Properties, mechanical properties, thermal conductivity

دراسة تأثير درجة الحرارة على الخواص التركيبية، الميكانيكية والتوصيلية الحرارة للبوليمر المتراكب (PVC / $CaCO_3$)

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الخلاصة

تم في هذا البحث دراسة الخواص التركيبية والتي تضمنت حيود الاشعة السينية (XRD) ومسعرية الحراري التفاضلي (DSC)، والخواص الميكانيكية والتي تتضمن اختبار الشد (Tensile Test)، اختبار الانحناء ثلاثي النقط (Bending Test) واختبار الصلادة (Hardness Test) والتوصيلية الحرارية (Thermal Conductivity) للمواد البوليميرية المدعمة بمادة الكالسايت (PVC/$CaCO_3$) كدالة لدرجة الحرارة، الدرجات الحرارية المستخدمة في هذا البحث هي °C (25–40–80–120–160–200–220). وقد أظهرت نتائج البحث ان درجة التبلورية (X_C) حيود الاشعة السينية تقل مع ارتفاع درجات الحرارة (220°C)، اما المسافة البينية للبوليمر المتراكب (PVC/$CaCO_3$) تزداد بأرتفاع درجة الحرارة، ونتائج اختبار المسعر الحراري التفاضلي (DSC) تبين أن درجة التبلورية (X_C) تقل بأرتفاع درجات الحرارة (220°C)، اما بالنسبة الى نتائج اختبار الفحوصات الميكانيكية فأنها تقل قيمها مع ارتفاع درجات الحرارة. وأخيرا فأن نتائج اختبار التوصيلية الحرارية تشير الى ان قيمتها تقل بأرتفاع درجات الحرارة (220°C).

Introduction

Polyvinyl chloride PVC is one of the most commonly used man-made polymers because of the unrivalled combination of properties that it offers. It is the ratio of economic cost to performance makes it immediately more accessible than most other materials and the diversity of ways in which it

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can be used challenges the imagination, from roofing membranes to credit cards, from children's toys to pipes water [1].

The PVC uses in many applications because of its excellent properties like low diffusion for humidity, high resistance to abrasion, high electrical insulation and good flexibility within a range of temperatures and resistance to water, bases, acids, alcohols, oils, and aliphatic hydrocarbon components (compounds) [2].

There are two important kinds of PVC [2]:

- Rigid PVC: which is used in fabrication of pipes and plastic plates (sheets).
- Flexible PVC: which is composed of polymer with the addition of plasticizers. This type of PVC used in the fabrication of films, coating purposes and production of industrial leathers.

X-ray diffraction (XRD) is a technique that measures the intensity into or out of materials 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 measure sheet 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 rationing against the heat of fusion for a 100% crystalline sample of the same material, or more commonly by rationing against a polymer of known crystallinity to obtain relative values [4].

The tensile test is popular since the properties obtained can be applied to design different components. The tensile test measures the resistance of a material to a static or slowly applied force. The strain rates in a tensile test are typically small [5].

In polymeric materials, this stress will correspond to disentanglement of polymer molecule chains or sliding of chains past each other. Tensile Strength the stress obtained at the highest applied force is the tensile strength, which is the maximum stress on the engineering stress-strain curve. This value is also commonly known as the ultimate tensile strength (UTS) [5].

Bending test is one of the basic test of composite material to determine the properties of elasticity. Wherc e the bending resistance of the material is the tolerance of the material for vertical bending force on its longitudinal axis, There is some important factors that effect of the bending test: type and load rate, the distance between the predators and the distance of the cross section of the sample[6].

The hardness test measures the resistance to penetration of the surface of a material by a hard object. It is a qualitative measure of the strength of the material The depth or size of the resulting indentation is measured, which in turn is related to a hardness number; the softer the material, the larger and deeper the indentation, and the lower the hardness index number [6].

Thermal conductivity can be defined as the amount of heat transferred within one second divided by the temperature gradient and its units are ($W.m^{-1}.k^{-1}$). Thermal conductivity varies from one substance to another. Metals are good conductors of heat. For example, copper has thermal conductivity up to (400 $W.m^{-1}.k^{-1}$), Polymer materials are heat-conductant materials with a conductivity of up to (0.3 $W.m^{-1}.k^{-1}$) or less.

Experimental Part:

Samples were thermally treated in a (Carbolite chamber furnaces with maximum operating temperatures 1200°C). The samples were placed in a non-vacuum furnace for 40 min under a certain weight, in order to prevent bending during the thermal treatment. Moreover, the temperatures were utilized in this study are: (25-40-80-120-160-200-220) ºC

1. Structural properties:

• X-ray diffraction (XRD):

X-ray diffraction scanning (XRD) was performed using Shimadzu XRD-6000 with monochromatic CuKα radiation at a scan speed of (0.02 deg.sec1) and the θ angle between 5 to70 degrees, all samples were made in the form of small rectangles with dimensions of (3 * 2 cm).

The degree of crystallization (X_C) is calculated by using following equation [7]:

$$X_C\% = \frac{I_c}{I_c+I_a} \qquad \text{……1}$$

$$X_c\% = 1 + \frac{I_c}{I_a} \qquad \text{……2}$$

$$X_c\% = \left(1 + \frac{I_a}{I_c}\right)^{-1} * 100\% \qquad \text{……3}$$

Whereas:
X_C = degree of crystallinity , Ic = density of crystalline region, Ia = density of non-crystallized region.
By application of the crystalline system equation of the hexagonal shape We can find the surface area as shown in:

$$\frac{1}{d_{hkl}^2}=\frac{4}{3}\left(\frac{h^2}{a^2}+\frac{hk}{a^2}+\frac{k^2}{a^2}\right)\frac{l^2}{c^2} \quad \ldots\ldots\ldots\ldots 4$$

- **Differential scanning calorimetry (DSC):**

Differential scanning calorimetry (DSC) was Performed on DSC (STA.PT.1000.plant) by company (LINSEIS) Germany. All samples were made in the form of small rectangles with dimensions of (3 * 2 cm), and 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 [7].

$$X_C\% = \frac{\Delta H}{\Delta H_\circ} * 100\% \quad \ldots\ldots\ldots\ldots 5$$

Where ΔH is the enthalpy of the sample and $\Delta H_\circ$ is the enthalpy of the totally crystalline to the same sample

2. Mechanical properties:

- **Tensile strength:**

The tensile behavior of samples was determined at (25-220 ˚C) using tensile testing machine model H50KT manufactured by (Tinius Olsen/UK). The samples were prepared in accordance with ASTM-D638. The specimen was loaded between two manually adjustable grips of a (2000 N) computerized tensile testing machine

The tensile strength (TS) has been calculated by using [8]:

$$\sigma = P/A \quad \ldots\ldots\ldots\ldots 6$$

where:
σ = stress (Mpa), P = applied load in the test (N), A = original area of the test specimen (mm)2.
The strain is given by eq (7):

$$\varepsilon = \frac{\Delta L}{L_\circ} = \frac{L-L_\circ}{L_\circ} \quad \ldots\ldots\ldots\ldots 7$$

Where: ε = strain, L = length at any point during the elongation mm, Lo =original gage length (mm).

Hooke's -Law, defines the stress – strain relationship:

$$Y = \frac{F/A}{\Delta L/L} \quad \ldots\ldots\ldots\ldots 8$$

Where: F= force, A= area, ΔL= change in length, L= Original length.

- **Flexural strength:**

Flexural strength is determined by 3-point bend test. The test specimen accordance with ASTM-D790 was used for the test. Using bending instrument model H50KT manufactured by (Tinius Olsen/UK). Flexural strength can be calculated using following Eq. (9)[8].

$$\delta_{max} = \frac{3\,f\,L}{2\,w\,h^2} \quad \ldots\ldots\ldots\ldots 9$$

δ max = Bending Stress (Mpa), f= the applied load (N), L= The distance between the supports (mm), w= width, (mm), h= thickness.

- **Hardness shore (D):**

The shore D hardness of the samples was measured using a Durometer device (fabricated by TIME GROUP INC Company) according to the ASTM (D 2583-67). The Durometer instrument has an indenter projecting below the base (face) of the pressure foot. The indenter was pressed with sufficient band force for 5 seconds into the plastic specimen perpendicularly so that the base took rest on the plastic surface. The amount of indentation registered directly on the dial indicator

3. Thermal conductivity:

Lee`s disc device, made by the (Griffen and George Company), was utilized to test the thermal conductivity of the samples under test. This device is composed of three discs of brass (40 mm diameter by 12.25 mm thickness) and a heater. The sample was put between the discs A and B, while the heater was put between B and C. Heater was supplied with a voltage (6 volt) and the current value through the device was about (0.25 A). The heat moves from the heater to the near two discs then to the third disc across the sample[9].

$$k\left[\frac{T_B-T_A}{ds}\right]=e\ \left[T_A+\frac{2}{r}\left[T_A+\frac{1}{4}ds\right]T_A+\frac{1}{2r}ds\ T_B\right] \text{.......} 10$$

where: K is thermal conductivity coefficient (W/m.K), TA, TB, and TC: are the temperatures of the disk (K) respectively. dA, dB, and dC: are the thicknesses of the disks (mm) respectively. dS: is the thickness of sample (mm)

r is the disk's radius (mm). e is the quantity of heat flowing through the cross sectional area of the specimen per unit time (W/m2. K), which is calculated from the following equation[9].

$$IV=\pi r^2 e(T_A+T_C)+2\pi re\left[d_A T_A+ds\left(\frac{T_A+T_B}{2}\right)+d_B T_B+d_C T_C\right] \text{.......} 11$$

Results and Discussion:

- **XRD:**

Wide-angle X-ray diffraction (WAXRD) has been applied in the crystal structure evaluation of composite material (PVC/CaCO3). Spectra of the polymers at diffraction temperatures are displayed in figure (1). Three clear peaks were observed in the spectra. Lattice parameters can be obtained using the equation no. (4) **[**10] , of the hexagonal lattice structure, results are listed in the Table-1.

Table 1-Miller indices (hkl) assigned for peaks in XRD spectrum for (PVC/$CaCO_3$).

2**θ** (deg)	d_{obs}. (°A)	d_{calc}. (°A)	Hkl
29.753	3.035	3.02946	(104)
47.7543	1.913	1.91066	(018)
48.8088	1.875	1.87245	(116)
36.3167	2.495	2.47173	(110)
39.7490	2.285	2.26585	(113)

We chose the intensity of the plane (104) as it has the higher intensity value than other peaks. It was noted that the intensity of the plane (104) decreases gradually as the temperature increased, this is because the polymer molecules composite (PVC / $CaCO_3$) are free to shrink during the thermal treatment. This leads to the free movement of the particles within the crystalline lattice. This indicates that the high temperature leads to the redistribution of some crystalline areas and this leads to appear other reflections sites [10].

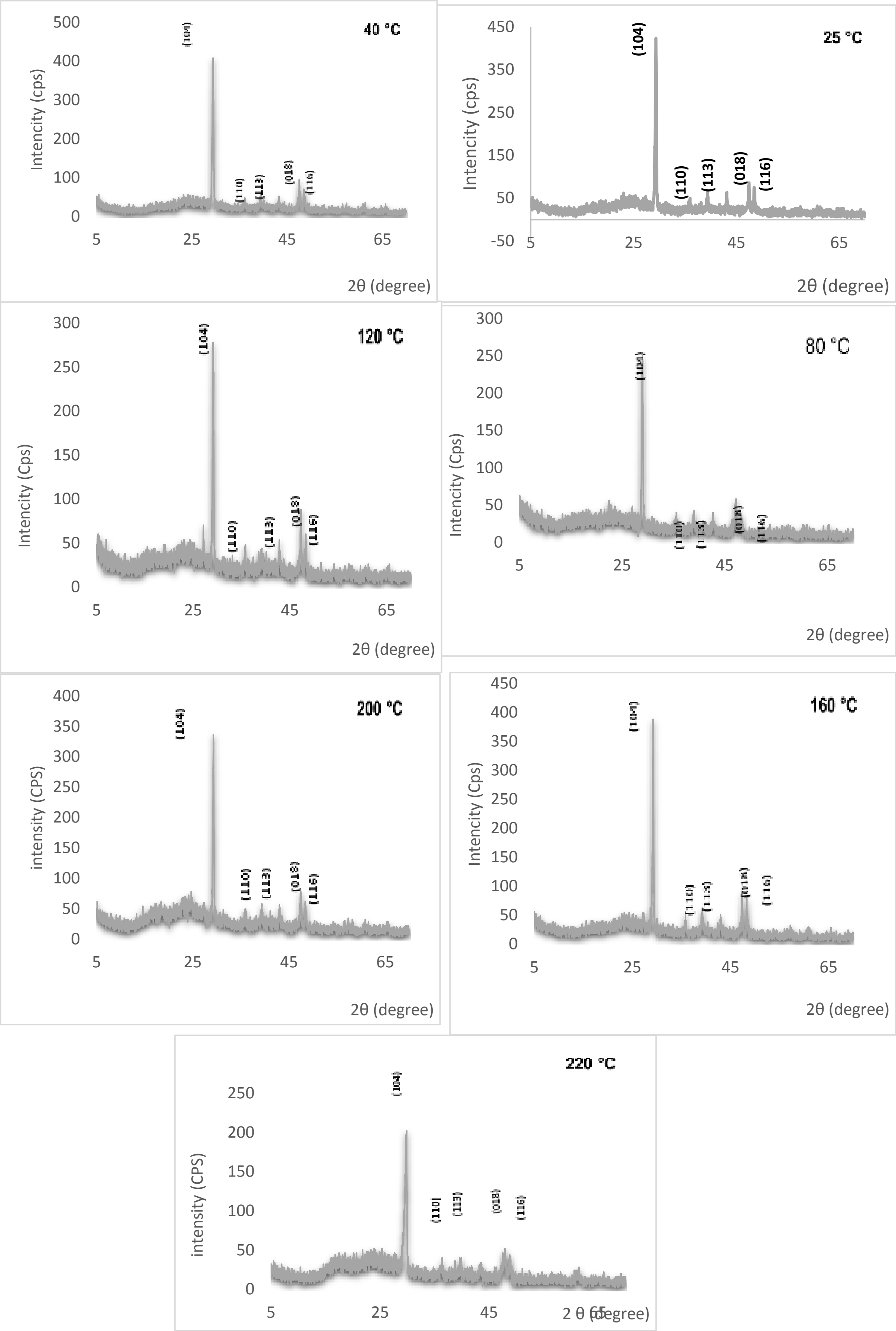

Figure 1- show the data of XRD-diffraction for PVC composites with different temperature.

The degree of crystallinity calculated from equation (3), from table (2), we observed that the degree of crystallinity (Xc) decreases gradually with increase temperature.

Table 2- The degree of crystallinity calculated by XRD for PVC/$CaCO_3$ Composite.

T(ºC)	I_a (CPS)	I_C (CPS)	X_C (%)
25	3649.8	5838	61.531
40	1760	2490	58.588
80	1745.7	2392	57.809
120	924	1220	56.902
160	422.4	458	56.471
200	988.9	1246	55.751
220	2255	2816	55.531

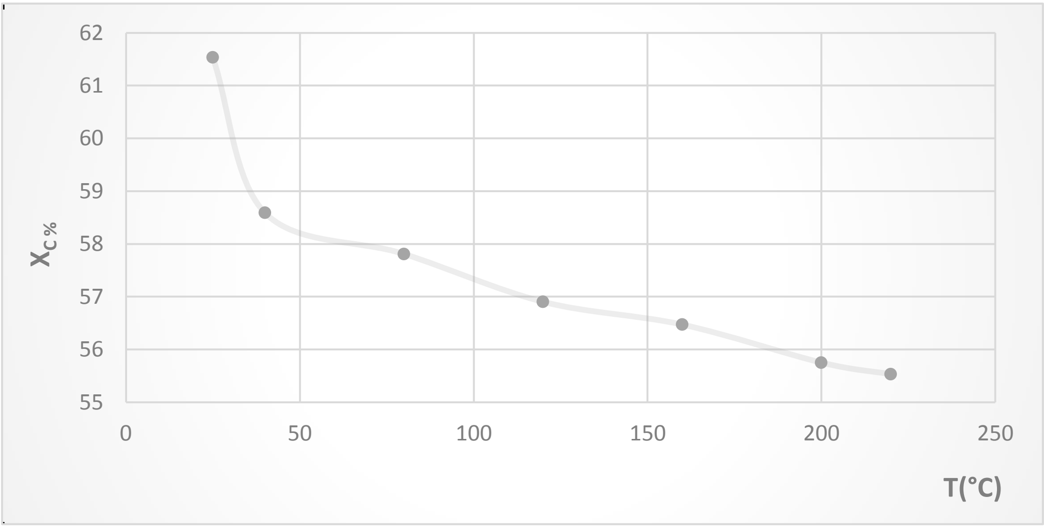

Figure 2- degree of crystallization decreasing with increasing temperature for PVC /$CaCO_3$ composites.

- **DSC:**

Figure-3 shows the enthalpy curve of Polymer composite (PVC/$CaCO_3$) as a function of temperature. Where, we observe a change in the slope of the curve at (81 ° C), which represented the glass transition temperature (Tg).As well as, the presence of a heat-absorbent peak at (260 ° C) which represented the melting point of the pure polymer. However, because of the effect of calcite on PVC, we notice that the glass transition temperature (Tg) and the polymer melting point (Tm) head for creeping. By using equation (5),the degree ofcrystallinity was calculated, based on (176) j/g of the 100 % crystalline of pure PVC [11].The resultsof the studied samples are summarized in Table-3

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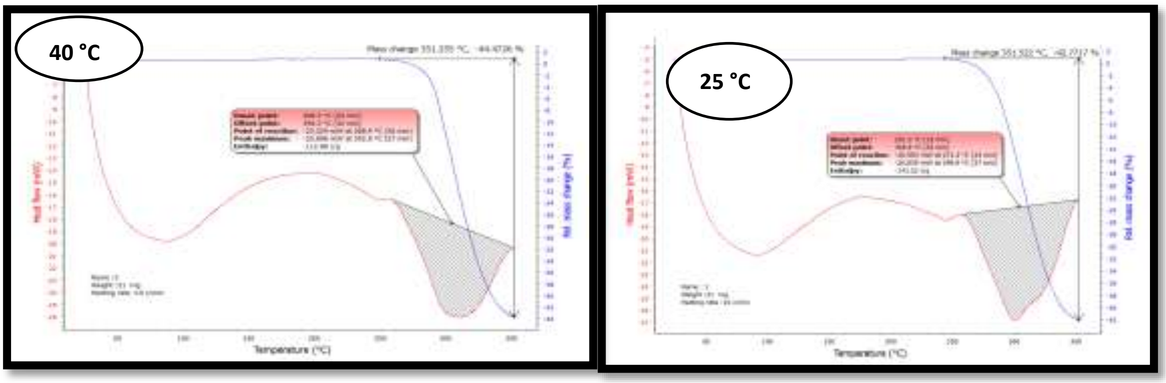


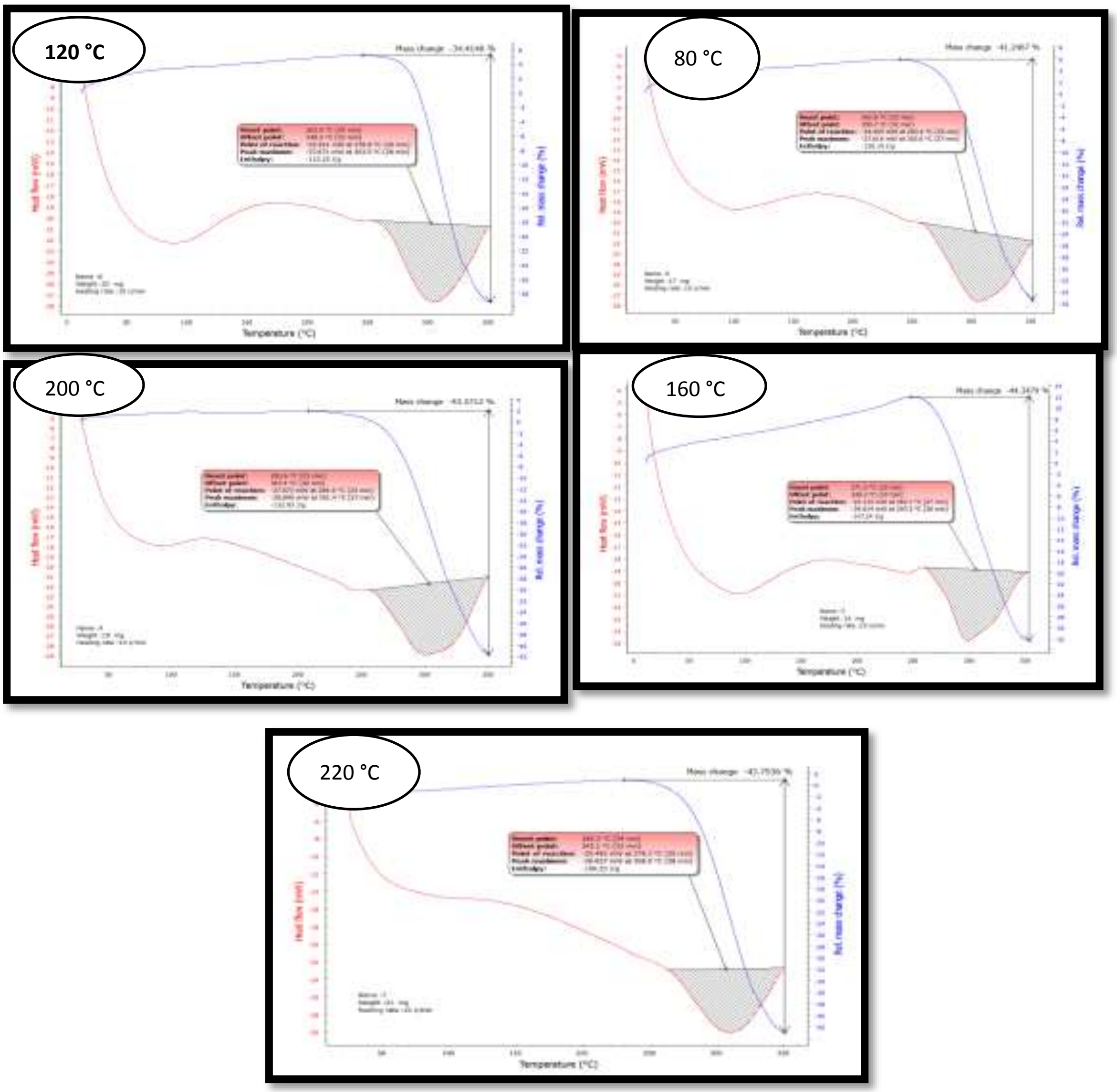


Figure 3- DSC curve of the PVC/$CaCO_3$ composite.

Table 3- DSC characterizations of PVC composite samples after heat treatment.

T(°C)	ΔH (J/g)	ΔH_o (J/g)	X_C (%)
25	143.52	176	81.54545
40	112.88	176	64.13636
80	107.24	176	60.93182
120	132.93	176	75.52841
160	128.1	176	72.78409
200	115.25	176	65.48295
220	106.3	176	60.35795

From Table-3, we found that the degree of crystallinity (Xc) decreases gradually as temperatures increased. This is due to the preparation method of the samples to be tested by the (DSC) technique, which requires placing samples inside a heat-resistant crucible and ensure that they are covered in a good contact with the whole sample to ensure the regular transferring of heat. Typically, DSC technique gives the results of the crystallization degree less accurately than other techniques such as XRD **[11]**. As illustrated in Figure-4.

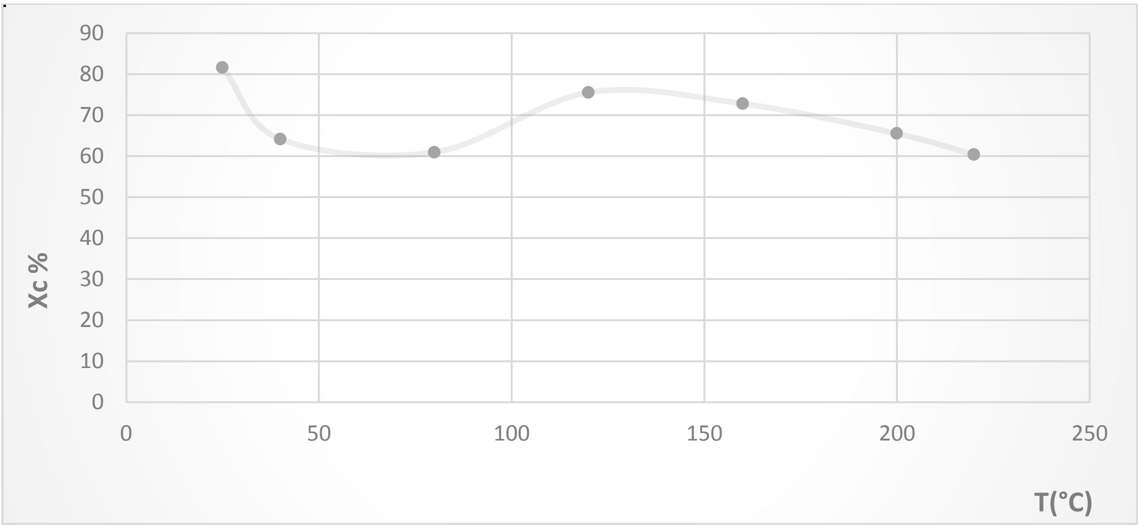


Figure 4- decreasing degree of crystallization with increasing temperature.

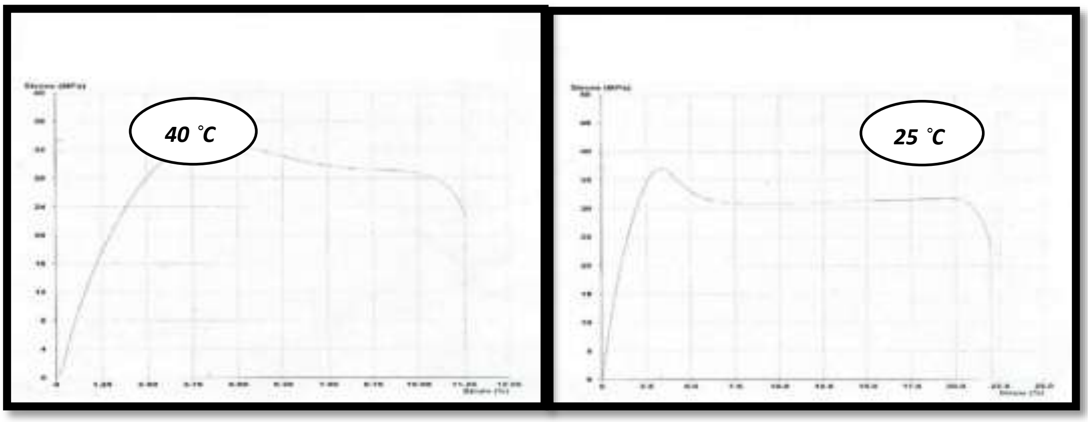
- **Tensile Test:**

Stress-strain curves of (PVC/Composites) as shown in Figure-5. From these tensile curves, we can get young's modulus, ultimate tensile strength, Stress at Break and Strain at Break, which listed in Table-4.

Table 4-tensile properties of PVC composite.

T(ºC)	Yong Modules (MPa)	Tensile Strength (MPa)	Stress at Break (Pa)	Strain at Break (%)
25	20	37.08	550	9.15
40	17.78	33.75	530	8.8
80	70.5	33.7	850	38
120	17.02	32.1	470	5.2
160	16	33.48	460	4.9
200	14.54	33.36	440	4.7
220	12.9	32.92	376	4.55

The results obtained from the stress-strain curve, as shown in the Table-4, that all the tensile test results decrease with high temperatures because the heat directly causes an increase of the strain, which is directly proportional to the temperature rise. Moreover, the elastic part of the stress-strain is increased, and thus reducing the brittleness of the samples and becoming more coherent.



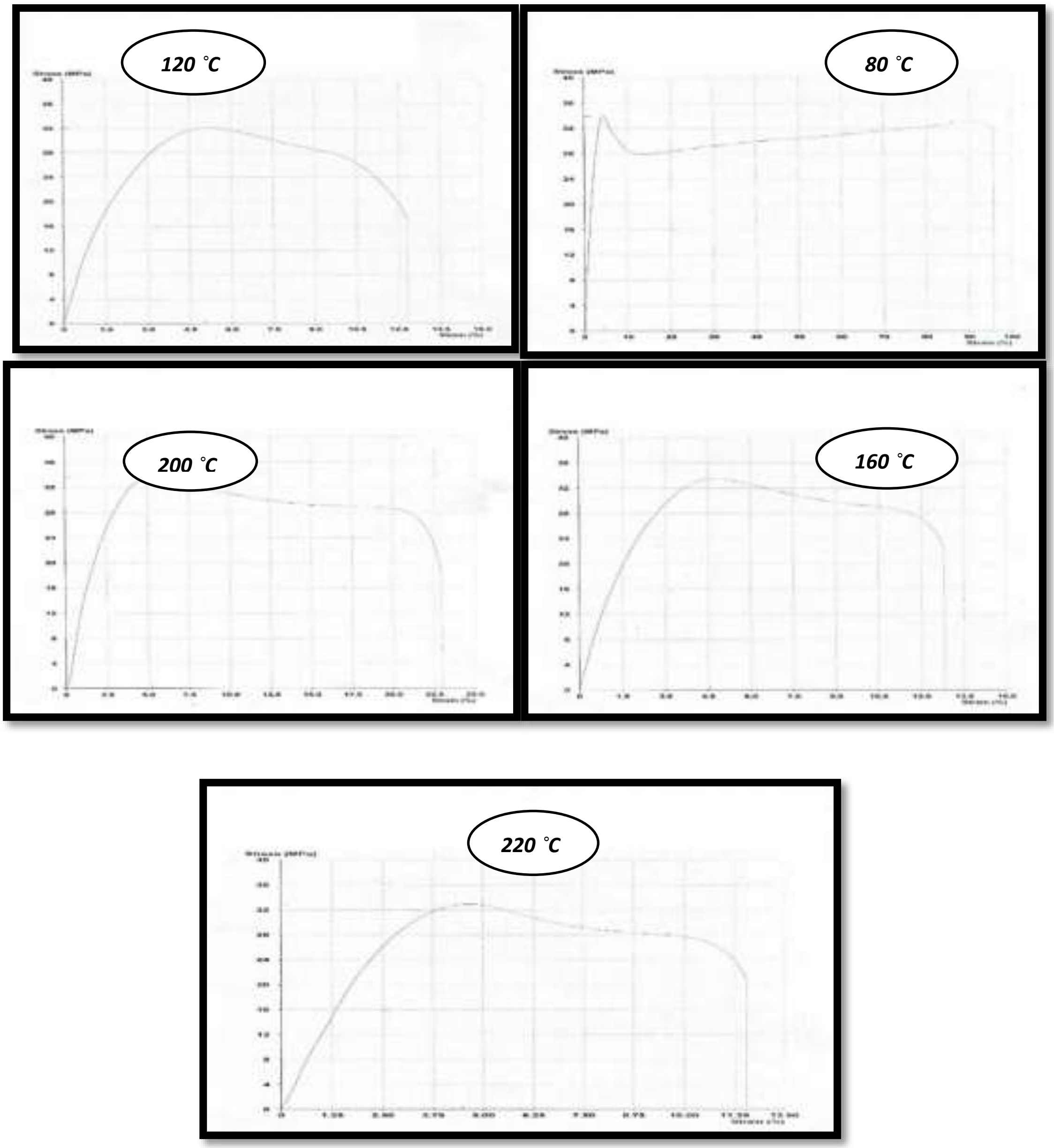


Figure 5-stress-strain curve for PVC composite at different temperature.

From Table-4 we can show the decrease in Young modulus with the increase of temperature because of the increase in stress with the increase in strain. 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 [7].

In another side, the stress at break and strain at break are decreased with the increase of temperature that is due to the decreased of orientation of the molecular chains for polymer.[11]

- Bending Test:

The Table-5 and Figure-6 by using equation (9) show the bending strength as a function of temperature change. The bending strength decreases as temperature increased. This may attribute to the increasing in temperature of the samples, and this leads to reducing the bonding forces between the molecular chains of the matrix material, and thus become flexible and a great strain occurs, where this leading to decreasing of bending strength.[12].

This difference in the flexural strength because there is the difference in the bonding between the chains[13]

Table 5- flexure strength as a function of PVC/CaCO3 composites.

T(°C)	F.S (MPa)
25	76.1
40	66.3
80	66
120	65
160	73.5
200	62.2
220	60.8

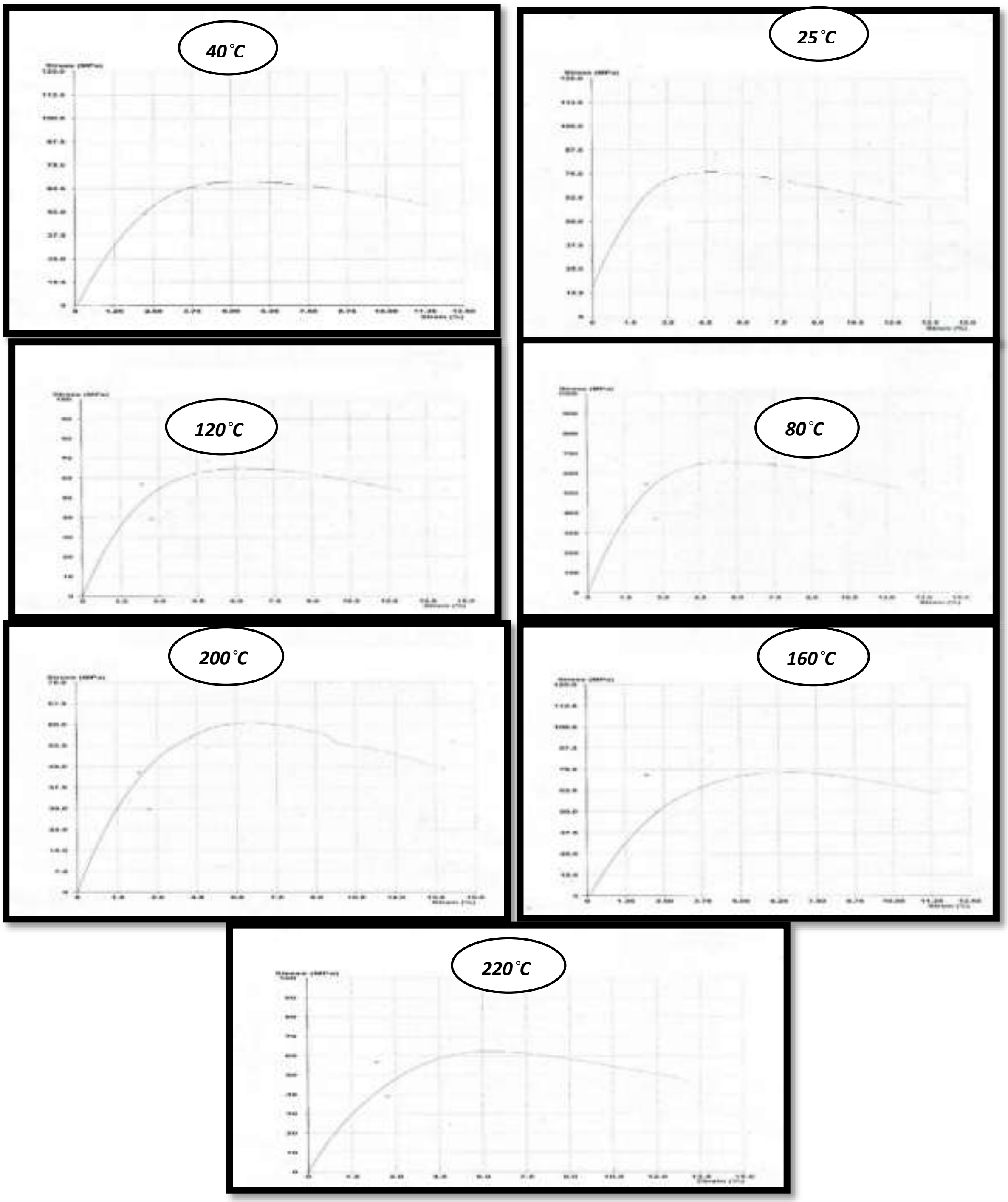


Figure 6- show the flexure strength at different temperature.

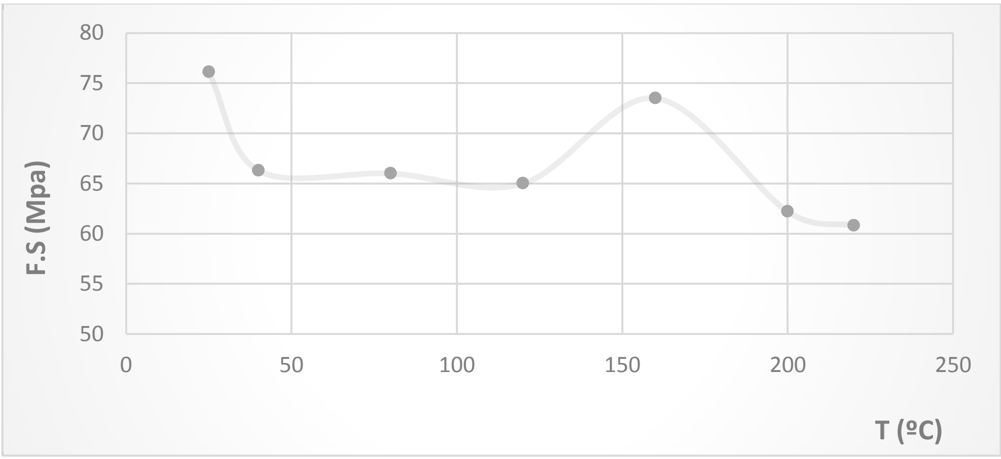


Figure 7- decreased flexure strength with increased temperature.

- **Hardness shore (D):**

Table-6 and Figure-8 show the effect of high temperature on the hardness of the (PVC / $CaCO_3$) composite material. It is observed that when the samples are exposed to different temperatures for 40 minutes that the hardness values have reduced at a high temperature this is because the increasing the temperature has led to increased flexibility of the material. This is due to the movement of molecules and breaks the bonds between them, and this leads to the weakening of their resistance to scratching and stitching.[14]

Table 6- hardness test at different temperature.

T(ºC)	Hardness Shore (D)
25	22.5
40	21.3
80	19
120	19.2
160	18.9
200	18.7
220	16.6

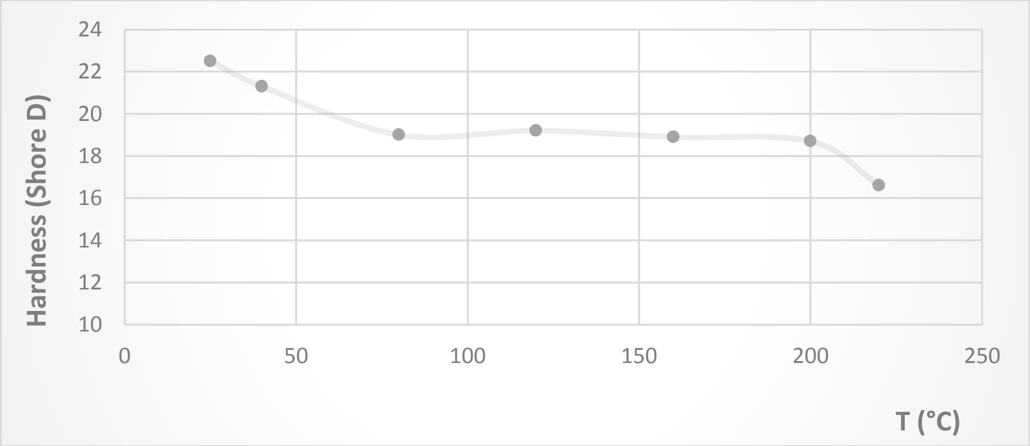


Figure 8- show the hardness of PVC /$CaCO_3$ composites as a function of temperature.

- **Thermal Conductivity:**

The thermal conductivity of solid insulation materials is carried out by phonons, where they are the only carrier of thermal energy. At high temperatures, phonons play the main role in thermal conductivity of all types of solid materials .[15]

The thermal conductivity of all the samples was calculated using the equation (10) and (11). The obtained results from the Table -7 have shown that the thermal conductivity was reduced at a higher temperature. From Table -7, it is possible to observe that the average thermal conductivity of these samples is less than (0.45W/m.k), which reflects a high resistance, to heat transfer. This means that they could be used as thermal insulators. The decrease in thermal conductivity is due to the reducing velocity of the photon and lack of free electrons [14], as shown in Figure- 9.

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Table 7- show that the thermal conductivity at a different temperature.

T(°C)	K (w/m.k)
25	0.00342
40	0.0024
80	0.00162
120	0.00135
160	0.00103
200	0.000855
220	0.00068

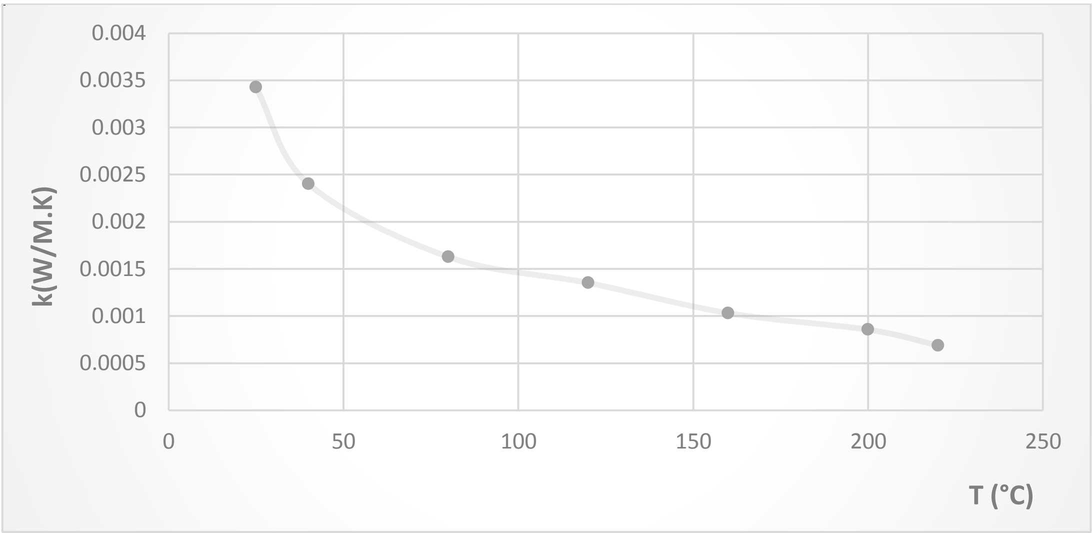

Figure 9-show that the thermal conductivity as function of temperature.

Conclusions

1- The degree of crystallinity (Xc) of the polymers reinforced with calcite (PVC/$CaCO_3$) as a function of temperature was calculated using X-rays diffraction and DSC techniques and it was observed to decrease as temperature increased.

2- All the mechanical properties that are included tensile test, three-point bending test (Bending Test) and hardness test were found to decrease with increasing temperature.

3- The thermal conductivity measurements as a function of temperature were indicated that the thermal conductivity values decrease as the temperature increased.

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