Non-Isothermal Crystallization Kinetics Model of PBT/ MWCNTs Nanocomposites

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ABSTRACT

The non-isothermal crystallization kinetics and crystalline properties of nanocomposites poly butyleneterephthalate, [PBT] /multiwalled-carbon nanotubes (MWCNTs) were tested by differential scanning calorimetry (DSC). PBT/(MWCNTs) nanocomposite was prepared by ultrasonicated of MWCNTs (0.5, 1, 2, 4 wt %) in dichloromethane (DCM) and after that the powdered PBT polymer was added to the MWCNTs solution. The non-isothermal crystallization results show that increasing the MWCNTs contents, decreased the melting temperature (Tm) of PBT/(MWCNTs) nanocomposite as compared with pure PBT, while resulting in improving the degree of crystallinity. These results indicated that a little amount of MWCNTs can be evident strong nucleating agent in PBT nanocomposites. Avrami kinetics model results given a good agreement with the frequent investigation. The Kissinger method shows the MWCNTs had a well nucleation effect on the crystallization of PBT, and the enhancement activation energy (Ea) with increased the MWCNTs in PBT/ (MWCNTs) nanocomposite.

Keywords: crystallization, kinetics, poly (butyleneterephthalate), carbon nanotubes, nanocomposites

نمذجة حركية تبلور البولي بيوتلين تيرفيثالات المدعم بأنابيب النانو كاربون المتعدد الجدران

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الخلاصة

تمت دراسة حركية وخواص التبلور لمركب البولي بيوتلين تيرفيثالات المدعم بالانابيب النانوية الكاربونية المتعددة الجدران باستخدام الماسح التفاضلي الكروموتوغرافي. تم تحضير المركب بنسب وزنية مختلفة من الانابيب النانوية الكاربونية. اثبتت نتائج حركية التبلور ان زيادة نسبة الانابيب النانوية الكاربونية تنقص من درجة حرارة الانصهار بالمقارنة مع البولي بيوتلين تيرفيثالات النقي بالاظافة الى تحسين درجة التبلور. هذة النتائج تبين التداخل الواضح للآنابيب النانوية الكاربونية في البوليمر. نموذج Avrami اعطاء نتائج جيدة ومطابقة مع البيانات العملية، كذلك نموذج Kissinger لحساب طاقة التنشيط اثبت ان زيادة نسبة الانابيب النانوية الكاربونية تزيد من طاقة التنشيط لحركية التبلور.

الكلمات الرئيسية : تبلور ،حركية، بولي بيوتلين تيرفيثالات. انابيب النانو كاربون ، مركبات نانوية

1. INTRODUCTION

Poly butyleneterephthalate is a traditional semi crystalline polymer and used in various engineering and electrical applications such as an insulator and housings, because of high rate of crystallization, hardness, thermal stability, and extremely good flow properties, **Mai, et al.,2006, Usuki, et al., 2005**.

Many researchers have been devoted toward the performance of crystallization and mechanical properties of PBT such as injection molding, **Xiao, et al., 2007, Kim, et al., 2006**, with different nanoparticles including carbon nanotube (CNT), **Kim, et al., 2009, Rejisha, et al., 2017**, organic clay **Saeed,** and **Khan, 2015, Chang, et al., 2005,** etc. The importance of the use of carbon nanotubes (CNT) in new types of nano scale polymer appeared where it adds enhancements for exceptional properties with high balanced amounts and little volume.

Carbon nanotubes (CNT) have been discovery by **Iijima, 1991**. Three types of nanotubes can be considered of minor importance which are: 1- single-walled carbon nanotubes [SWCNTs], 2- multi-walled carbon nanotubes [MWCNTs] and 3- double-walled carbon nanotubes [DWCNTs]. A multiwall carbon nanotubes (MWCNTs) are made up of various layers of carbon tubes having a common axis, with diameters from (10 – 50) nm and length above than 10 mm.

A well dispersed and entrenched were observed by functionalized carbon nanotubes (FCNT) inside PBT polymer by solution casting technique, which consequently led to make efficient properties of the nanocomposite such as the mechanical and thermal ones when compared with a neat PBT, **Saeed and Khan, 2014**.

Rejisha, et al., 2014. evaluated the action of (MWCNT) on the properties of poly butyleneterephthalate(PBT)/polycarbonate (PC) blends. The authors showed that small amount of MWCNT shows better rise in the properties of the blends of PBT/PC nanocomposite when compared to nanoclays or inorganic fillers.

Recently, solution casting technique was used to get (kaolin clay/PBT) composites films by **Saeed, and Khan, 2015**.The product showed that the supplements of clay polymer matrix were significantly better on the module and tensile strength of [PBT] polymer matrix, and when combination of clay into matrix, the dimensions of sphere ulites of PBT were reduced.

In the present work, the effect of MWCNTs on the crystalline properties of PBT was investigated. In addition, the non-isothermal crystallization kinetics behaviors of PBT/ (MWCNTs) nanocomposite were carried out using differential scanning calorimetry (DSC).

2. EXPERMENTS
2.1 Materials

The PBT was purchased from (Shenzhan Plastic Company China). The Multi walled carbon nanotubes (MWCNTs) (purity >95 %) was supplied from Shenzhen Company. The solvent dichloromethane (DCM) was obtained by Merc Company.

2.2 Sample Preparation

The different weight percentage of MWCNTs solution (0.5 - 4 wt %) was prepared by adding MWCNTs to dichloromethane and ultrasonicated with ultrasonic cleaning bath for 90 min at ambient temperature. After that the PBT polymer was added to prepare MWCNTs solution. Finally, the produced PBT/(MWCNTs) nanocomposite was stirred at 1500 rpm for 30 min.

2.3. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is a primary technique for measuring the PBT/ (MWCNTs) nanocomposite crystallinity and melting points. The DSC test is proceeding under the gas flow rate of nitrogen with a heating rate about 20 ^{o}C/min using SETARAM, 131 EVO, France instrument as shown in **Fig. 1**. Through the test, the variance for heat flow between the sample and reference is registered by a computer. Depending on the DSC operating conditions, the test is held for about 1 hour. When making changes in phase are detected, where the exothermic changes such as crystallization, cross-linking and oxidation represented the upward peak while the endothermic changes such as glass temperature (T_g) and melting temperature (T_m) represented the downward peak on the DSC diagram.

3 REUSELTS AND DISCUSSION
3.1 Non-Isothermal Crystallization Method

Non-isothermal crystallization kinetics as well as crystalline behavior of PBT/MWCNTs nano composite were scrupulous by utilized (DSC) test at a given heating and cooling rates. From (DSC) tests, the parameters for the melting enthalpy (ΔH_m), peak for the crystallization temperature (T_p) and for the melting temperature (T_m) can be obtained.
The crystallinity percentage (X_c) can be calculated from:

$$X_c = \frac{\Delta H_m}{\Delta H^o} \times 100 \tag{1}$$

The theoretical value for the heat of fusion for 100 % crystal PBT (ΔH°=140 J/g) was acquired and listed in **Table 1**, **Sabu T. and Visakh P**. **2011**.
The DSC curves for virgin PBT as well as PBT/MWCNTs nanocomposites are illustrated in **Fig. 2 (a and b)**. It is obvious that the peak crystallization temperature (Tp) of virgin PBT at 190 °C, while the Tp for PBT/MWCNTs nanocomposite has moved to a high temperature (200–203 °C). These results indicate that the MWCNTs represent professional nucleating agent for the PBT nanocomposite crystallization rate as compared with the virgin PBT polymer.

Fig. 2-b depicts the second scan DSC for the virgin PBT as well as PBT/MWCNTs nano composites samples. It was found that increasing the MWCNTs contents resulted in melting

temperature (Tm) decrease as compared with pure PBT. **Table 1** shows the result in enhancement the degree of crystallinity (Xc). In context, it has been revealed that 1 wt% MWCNTs gives an 11 % higher crystallinity of PBT/MWCNTs nanocomposite than its pure PBT, these resulted specified the appearance of nucleation PBT crystallization in the nanocomposite, this is due to the interaction between surface treated MWCNTs nanoparticles and the PBT segments. **Saligheh,** and **Forouharshad, 2011**.

In addition, when the stacking of nanotubes is little, the portability of the PBT macromolecular chains can be improved in this way, the crystallization rate and level of crystallinity of the PBT samples expanded, when the substance of nanotubes expanded, the fillers began to hinder the activation of the PBT macromolecular chains and keep macromolecular sections from acquiring request arrangement of crystal lattices cross sections. Hence, the fuse of a little amount of MWCNTs could adequately upgrade the crystallization of the PBT nanocomposite through heterogeneous nucleation, **Saligheh,** and **Forouharshad, 2013**.

3.2 Crystallization Kinetics Model

The crystallization kinetics analyzing for the polymer materials can be demonstrated by Avrami model. Relative crystallinity (X_t) can be connected with crystallization time (t) by the suggested   model, **Fanfoni, M. and Tomellini M., 1998**:

$$1 - X_t = \exp(-Kt^n) \tag{2}$$

Or,

$$\ln(-\ln(1 - X_t)) = (n \ln t) + (\ln K) \tag{3}$$

Where dH/dt is enthalpy rate and equation (4) can be used to calculate X_t:

$$X(t) = \int_0^t \left(\frac{dH}{dt}\right) dt \bigg/ \int_0^\infty \left(\frac{dH}{dt}\right) dt \tag{4}$$

Accordingly, figure (3) shows the relation of relative crystallinity with crystallization time of pure PBT as well as PBT/MWCNTs nanocomposites. It seems that the PBT/MWCNTs nanocomposites require less crystallization time to approach the same relative crystallinity at different rates of cooling as compared with pure PBT.

Fig.4 shows the relation of ln (-ln(1-Xt)) with ln(t) of the pure PBT as well as PBT/MWCNTs nanocomposites according to equation (3) will give the slope (n), the Avrami index, and the intercept, ln(K). Table (2) shows the kinetic parameters for the samples of the nano composites. The parameter of Avrami index (n) describes the growing mechanism and geometry of crystallization, and the parameter ln(K) describes the growth rate under the non-isothermal crystallization process.

From **Table 2**, it can be seen that the Avrami index (n) values for pure PBT are larger than that of PBT nanocomposites. Similar values were also reported by some researchers for PBT within the range of $(3.0 - 4.0)$. Apparently, the (n) value decreases with the MWCNTs content which shows that MWCNTs nanoparticles gives a good nucleating agents for PBT, **Hu,et al., 2008.**

3.3 Activation Energy For PBT/MWCNT Nanocomposites

    The thermal dynamic examination will provide the data of polymer intraparticles. Kissinger strategy may be the ultimate regularly utilized, through the activation energy of non-isothermal crystallization that can be effectively gained**, Kim, 2011**.

    The equation below shows the fundamental form of Kissinger equation, where (β) the cooling rate, (T_p) the peak temperature, (Ea) the activation energy and (R) the gas constant. **Zhiying et al., 2014.**

$$\ln\left(\frac{\beta}{T_p^2}\right) = \text{const.} - \frac{Ea}{RT_p} \tag{5}$$

Fig. 5 shows the test of Eq. (5) by plotting $\ln(\beta/T_p^2)$ with ($1/T_p$). From the straight line and taking the slope, Kissinger activation energy (Ea) for PBT-MWCNTs nanocomposites can be determined. The Ea values for PBT-MWCNTs nanocomposites at different MWCNT nano particles are shown in **Fig. 6**. It is clearly noticed the Ea values of all composites samples are higher than the pure PBT. It has been revealed that 4 wt% MWCNTs gives an 10 % higher Ea of PBT/MWCNTs nanocomposite than its pure PBT. This is a good signale that MWCNTs nanoparticles own well nucleation results on the crystallization of PBT/MWCNTs Nanocomposites, **Kim, et al., 2005**.

4 CONCLUSIONS

    PBT/(MWCNTs) nanocomposite has been successfully synthesized by ultrasonicated of MWCNTs (0.5, 1, 2, 4 wt%) solution in PBT polymer. (DSC) analysis were utilized to investigate the kinetics for PBT/ (MWCNTs) nanocomposite as non-isothermal crystallization. A little amount of MWCNTs can evidently be a strong nucleating agent in PBT nanocomposites. On other hand, Avrami kinetics model results had given a good agreement with the frequent investigation and the existence of MWCNTs in PBT/(MWCNTs) nanocomposite gives an 10 % higher increases of the activation energy (Ea).

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NOMENCLATURE

E_a = activation energy, kJ/mol.

K   =crystallization rate constant, min $^{-1}$.

n   =avrami index, dimensionless.

R   =gas constant, J /mol. K.

t   =crystallization time, min.

T_g =glass Temperature, ^{o}C.

T_m,   =melting Temperature, ^{o}C.

T_p =peck Crystallization Temperature, ^{o}C.

X_c =crystallization percentage, dimensionless.

X_t =relative crystallization, dimensionless.

β =cooling rate, ^{o}C/min.

ΔH_m =melting enthalpy, J/g.

ΔH^o =heat of fusion for 100% crystal of PBT, J/g.

Table 1. Data of PBT and PBT/MWCNTs Nanocomposite for Nonisothermal crystallization.

Cooling rate (^{o}C/min)	5	10	20	40	At 10 ^{o}C/min		
Sample	T_p(^{o}C)				T_m, (^{o}C)	ΔH_m (J/g)	X_c (%)
Neat PBT	190.00	183.50	175.72	165.80	224.6	50.13	35.81
PBT/(0.5 wt%)MWCNTs	197.02	190.30	182.51	172.02	224	53.01	37.86
PBT/(1 wt%)MWCNTs	199.10	192.41	184.80	174.54	223.6	55.67	39.76
PBT/(2 wt%)MWCNTs	202.00	195.20	187.72	177.18	223.8	55.55	39.68
PBT/(4 wt%)MWCNTs	205.05	198.37	190.63	180.51	223.5	54.83	39.16

Table 2. Parameters come by Avrami kinetics model.

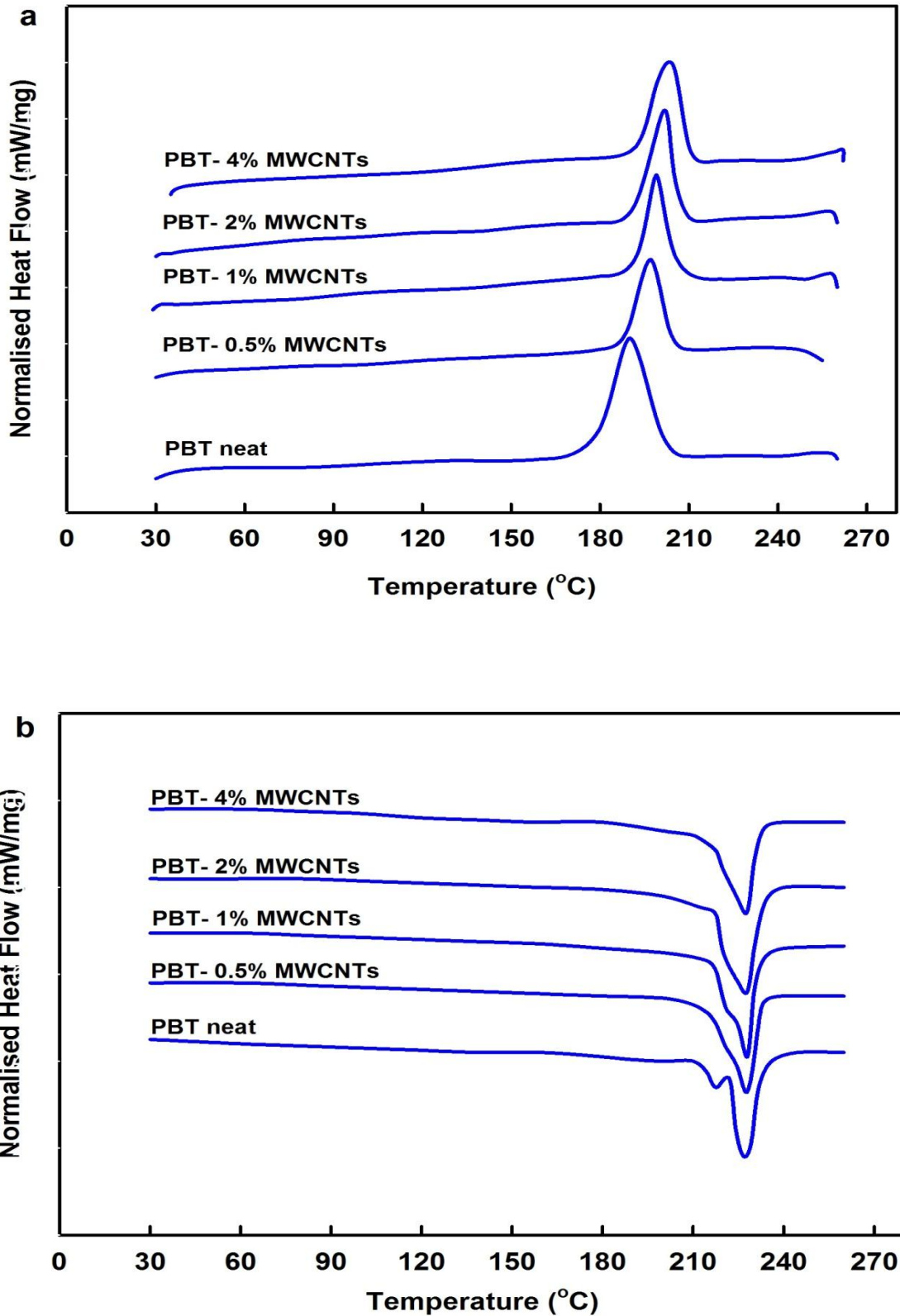| Test Samples	n	K×10²
Neat PBT	3.0303	0.726854
PBT/ (0.5 wt. %) MWCNTs	2.7504	0.941266
PBT/ (1 wt. %) MWCNTs	2.3065	5.269683
PBT/ (2 wt.%) MWCNTs	1.7968	16.05741
PBT/ (4 wt. %) MWCNTs	1.5786	30.09233

Figure 1. DSC SETARAM, 131 EVO instrument.

Figure 2. (DSC) trace for electrospun PBT/MWCNTs nanocomposite. (a) Non-isothermal crystallization for nanocomposite, (b) 2[nd]scans of nanocomposite.
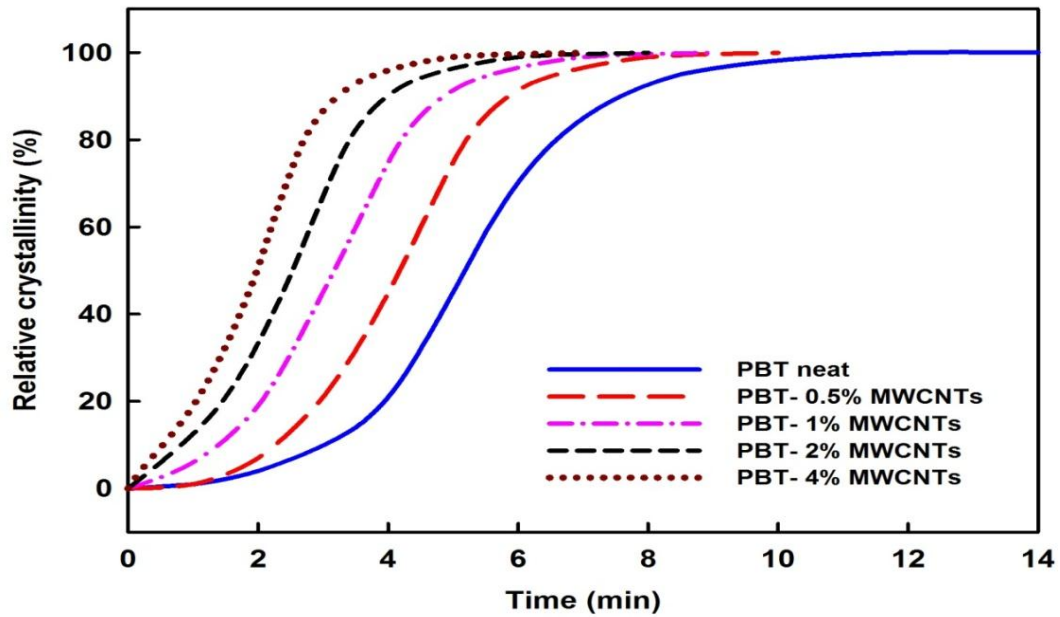
Figure 3. Divergence of relative crystallinity together with crystallization time. (Pure PBT as well as PBT/MWCNTs nanocomposites.)
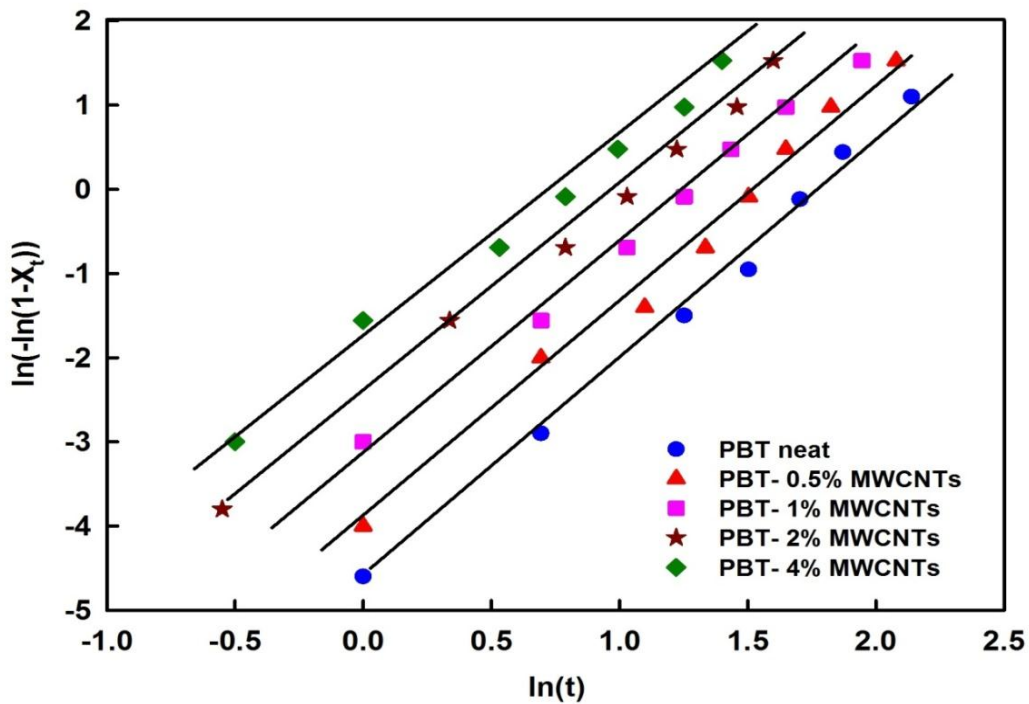

Figure 4. Plots of ln (-ln (1-X_t)) vs. ln (t). (Pure PBT as well as PBT/MWCNTs nanocomposites.)
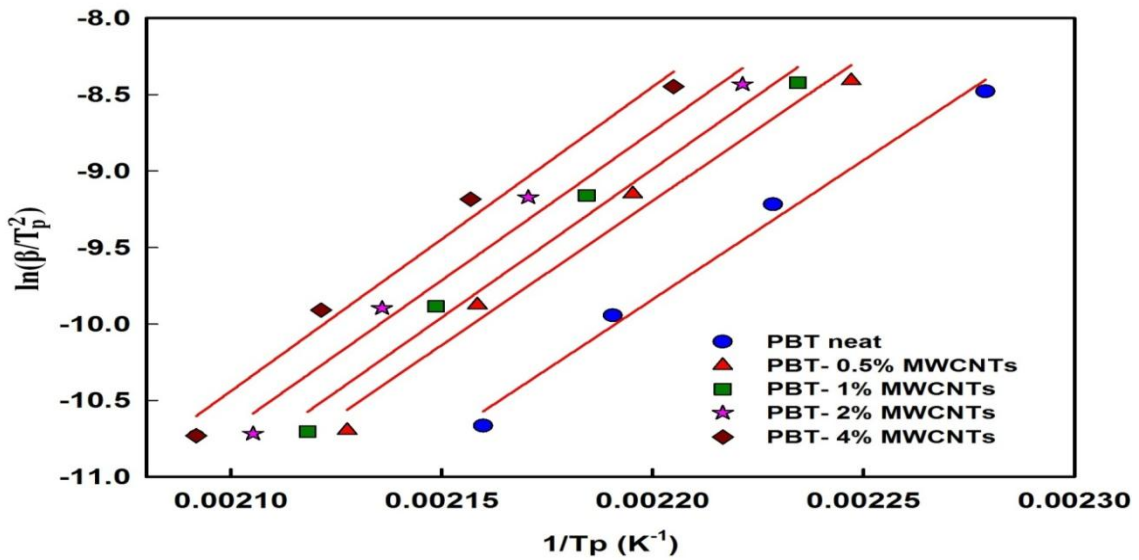
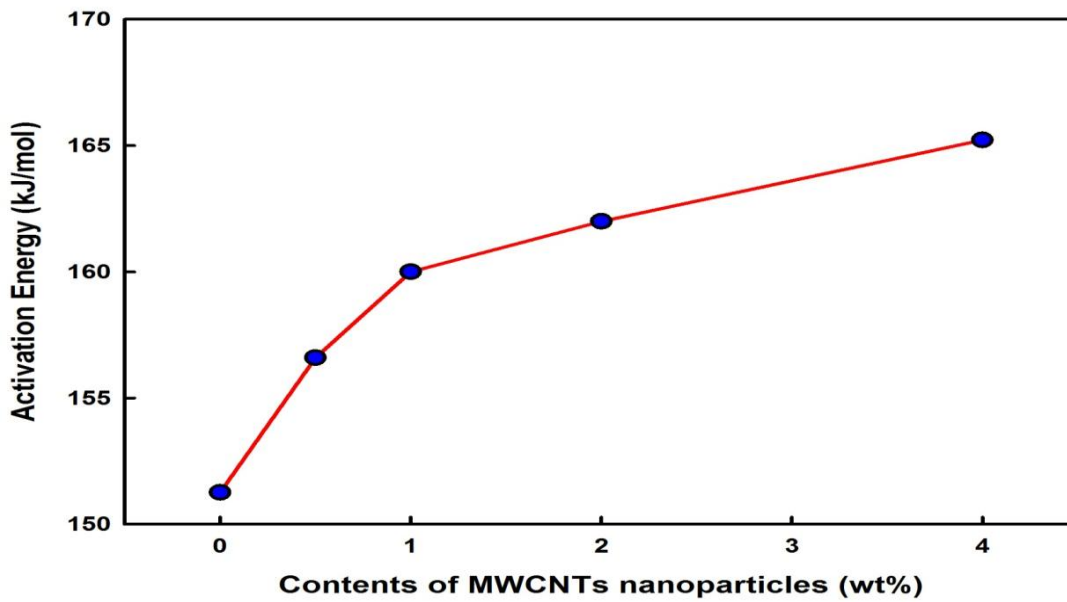**Figure 5.** Influence of $\ln(\beta/T_p^2)$ on $(1/T_p)$. (Pure PBT as well as PBT/MWCNTs nanocomposites.)

Figure 6. The Ea values for PBT/MWCNTs nanocomposites at different MWCNT nano particles.