



Thermal degradation mechanism of HDPE Nanocomposites containing Nano CaCO_3

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Abstract

In this study high-density polyethylene (HDPE)/ maleic anhydride grafted polyethylene (PE-g-MA) nanocomposites, containing 1, 3, 5 wt.% of CaCO_3 nanoparticles were provided by melt mixing process. Attendance of nanoparticles in PE matrix and addition of PE-g-MA led to enhancement of thermal stability of nanocomposites which proved by TGA analysis. In addition, kinetics of thermal decomposition of HDPE and its nanocomposites were examined. Addition of nano-particles led to enhancement of activation energy and degree of conversion.

Keywords: Nanocomposite, Kinetic thermal degradation, HDPE, Activation energy, Degree of conversion

Introduction

Polyethylene thermoplastic resin is world's most widely used plastic for many routine applications such as packaging industries, Pipe and fitting manufacturing, etc¹⁻². HDPE has many advantages such as good flexibility, resistance to chemical materials, low cost, high impact and toughness strength^{2,3}. One of the largest markets of HDPE is in pipe industries which can be used in agriculture, water supply and gas transition lines. PE water pipe has several advantages, such as light weight, high performance to price, reliable thermal stability, excellent chemical resistance, simple installation, as well as long term service time¹⁻³. PE100 and PE80 have the highest consumption as raw material in pipe industries^{3,4} especially for pressurized water pipes. These grades have low melt flow index (MFI), low permeability and also low thermal stability. For this reason, there is remarkable interest to address how thermal degradation has an effect on thermal and mechanical behaviors of PE pipe. This is partially related to the fact that the academic attempts on the mechanism of thermal degradation of PE pipe are very rare^{5,6}. It is very difficult to exactly find out the degradation mechanism of polyolefin pipe as both hydroperoxide formation and decomposition can take place in the same time during degradation. Long-term exposure to a high temperature causes to detrimental effects on thermal and mechanical properties. In addition surface morphology of PE pipe can affect as a result of thermal degradation. Generally, with increment of ageing time an enhancement in molecular weight, chain scission and crystallinity could be happen. Furthermore hydroxyl content and vinyl group would be enhance and more surface cracks could be observe, meanwhile antioxidant contents will be reduce and amorphous regions could become more clear⁷. Most common techniques⁸ can be utilized to investigate the oxidative degradation of polymers. Fourier transform infrared spectroscopy (FT-IR), can be used in order to measure changes

in hydroxyl and carbonyl oxygen based functional groups. Thermogravimetric analysis (TGA) also can be utilized for understanding the kinetics of the polymer decomposition. Differential scanning calorimetry (DSC) can be used to finding out changes that can be happen in melting point of polymer melting, crystalline temperatures and crystallinity. Wu et al. investigated non-isothermal thermogravimetric analysis measurements and calculated the activation energy and reaction orders are 233.2 and 0.74 kJ/mol⁹. K. Chrissafis and et al. studied degradation (thermal) of HDPE/SiO₂ nanocomposites by measuring their weight loss during heating and shown the activation energy for nanocomposites 61 kJ/mol more than pure HDPE also reaction order enhanced from 0.9 to 0.97⁴. Park and et al. used a new method for finding out the kinetic analysis of thermal degradation of several types of polyethylene. Thermal degradation of LDPE, LLDPE and HDPE estimated, and 219.2, 187.5 and 333.2 kJ/mol respectively and reaction order enhanced with growth of branching¹⁰. Backhorn and et al studied the mechanism and kinetics of polymers from isothermal and dynamic method. They found that activation energy of PE is about 262 kJ/mol and reaction order was 0.83¹¹. Kim and et al used DTG curves to investigate the kinetic parameters. They obtained different methods for investigating the reaction order and activation energy of HDPE¹². Addition of mineral fillers to polymeric matrix is mostly use to decrease production costs and in order to enhance the properties of the plastics, such as, strength, rigidity, flexural modulus and hardness. In some areas mineral fillers can cause a little improvement in thermal properties of polymers¹³⁻¹⁵. In highly filled thermoplastic systems, incompatibility between nonpolar polymer matrix and a polar can cause non uniformity in several properties as a result of inferior dispersion of the filler in the polymeric matrix. For solving this challenge, compatibilizer usually added to enhance the reaction between filler and matrix. This method can enhance interfacial adhesion in between

polymer and filler and can improve the mechanical properties¹⁵⁻¹⁷. PE-g-MA is the most commonly use coupling agent as it motivate the formation of covalent bond between the anhydride carbonyl and the hydroxyl groups on the surface of the fillers. For this reason addition of these types of coupling agents can enhance the compatibility of the filler with the polymeric matrix and subsequently better dispersion of filler, especially in nanoscale filler types.

In this research we investigated the effect of nano CaCO₃ and compatibilizer (PE-g-MA) on thermal degradation of HDPE/nano CaCO₃ nanocomposites.

Material and Methods

Materials: HDPE pipe grade (EX3) was supplied by Amirkabir petrochemical (Bandar Imam, Iran). Melt flow index (MFI) of HDPE is about 0.45 g/10min at 5 kg/190°C with the melting point about 125°C. Nano-CaCO₃ with 40 nm particle size used as a nanofiller and supplied by Omya pars Company, Tehran, Iran. Maleic anhydride grafted polyethylene- copolymer, used as a compatibilizer (density: 0.92 g/cm³), supplied by Kimia Javid Sepahan Co, Iran.

Sample preparation: Raw materials were dried at 80°C for 8 hours in vacuum oven. Nanocomposite samples were prepared by internal mixer (Plasticorder-PL2000, Brabender). Firstly, HDPE was molten in i mixer at 200°C for 5 min and then the compatibilizer added to molten matrix and mixed for 3 min. Nano CaCO₃ added to compound and mixing continued for 5 min. The discharged samples were cooled down and sheet type samples (1 mm thickness) prepared by hot press at 210°C for 5 min. The ratio of HDPE and compatibilizer were fixed at 85/15 by weight and detailed mass ratio was listed in table-1.

Table-1
Detailed mass ratio of samples

Sample	HDPE (Wt%)	MA-g-PE (Wt%)	NanoCaco ₃ (Wt%)
1	100	0	0
2	85	15	0
3	85	15	1
4	85	15	3
5	85	15	5

Characterization and Analysis: The FTIR spectroscopy was performed on the all samples using (Equinox55 FTIR spectrometer) to obtain absorbance spectra against wavenumber (cm⁻¹). Films were prepared by hot press instrument at 190°C for 2 min.

Thermogravimetric analyses of composites were done using TGA-7HT (Perkin & Elmer- USA) in the range of 30-600°C (5 °C/min, N₂ atmosphere).

Crystallization behavior of the samples was investigated by differential scanning calorimeter (Perkin Elmer DSC-1). The instrument was calibrated using indium (sample weight: 10 mg, N₂ atmosphere). All samples were heated up to 200°C and kept in the molten state for about 5 min to limit the influence of thermal history. The melts were then subsequently cooled at a rate of 10 °C/min to reach the considered temperature and kept at that temperature for about 1 hr. After completing the crystallization process, the samples were heated up to 200 °C (10 °C/min) to measure the melting temperature.

To study the microstructure of HDPE/nano CaCO₃ nanocomposites, a scanning electron microscopy (Philips XL30-Netherlands) was utilized to study the cryogenically fractured surface.

Results and Discussion

As we know, HDPE filled with CaCO₃ particles is highly brittle. In order to gain appropriate interface adhesion between the HDPE as a polymeric matrix and the CaCO₃ as a filler, two methods are possible: One is to chemically modification of HDPE, and the other one is surface treatment of the filler. So in this research was tried using compatibilizer and nano CaCO₃ with surface treatment.

The strength of the nanocomposites is usually due to the nano size distribution in nanocomposites and good interaction between modified nano CaCO₃ and HDPE with compatibilizer, in this nanocomposites nano Caco₃ with surface treatment is the hydrophilic material, but HDPE is a hydrophobic base material and as a result of different polarities, interfacial adhesion between mineral nano fillers and HDPE matrix is not well enough to gain acceptable properties. In order to overcome this problem MA-g-PE used as a compatibilizer to raise interfacial adhesion, between filler and matrix. FTIR spectra of nano CaCO₃ shown in figure-1, -CH₃ and -CH₂ stretching bands (absorption) is obvious at a 2920 cm⁻¹. This peak is related to attendance of organic compound which grafted onto the surface of nano fillers as a result of attendance of oxygen atom in -COOH or -OH that could confirm a coordination bonds with the Ca⁺² in CaCO₃. FTIR spectra of Nano CaCO₃, pure HDPE, PE-g-MA and HDPE/NanoCaCO₃/MA-g-PE. With addition of compatibilizer the ester forming was created. Absorption peak at 1740 cm⁻¹ is characteristic band of the stretching vibration of C=O, when compatibilizer add to polymer matrix C=O bond created. By addition of nano with compatibilizer to polymer matrix dipole-dipole interaction was created.

There are two reason for using MA-g-PE as a compatibilizer: i. The ability of ester formation of anhydride groups with hydroxyl groups in surface treatment of nanofillers, and the ability for formation of hydrogen bonds between the carboxyl groups of hydrolyzed maleic anhydride and hydroxyl groups on which located on the surface of treated Nano CaCO₃; ii. Fine

compatibility in between MA-g-PE chains and the HDPE phase that formed by physical entanglement.

HDPE by using PE-g-MA compatibilizer. As is clear from reaction chemical interaction between nano and PE-g-MA was created and physical entanglement among HDPE and compatibilizer was occurred.

Scheme 1 was shown interaction between nano CaCO_3 and

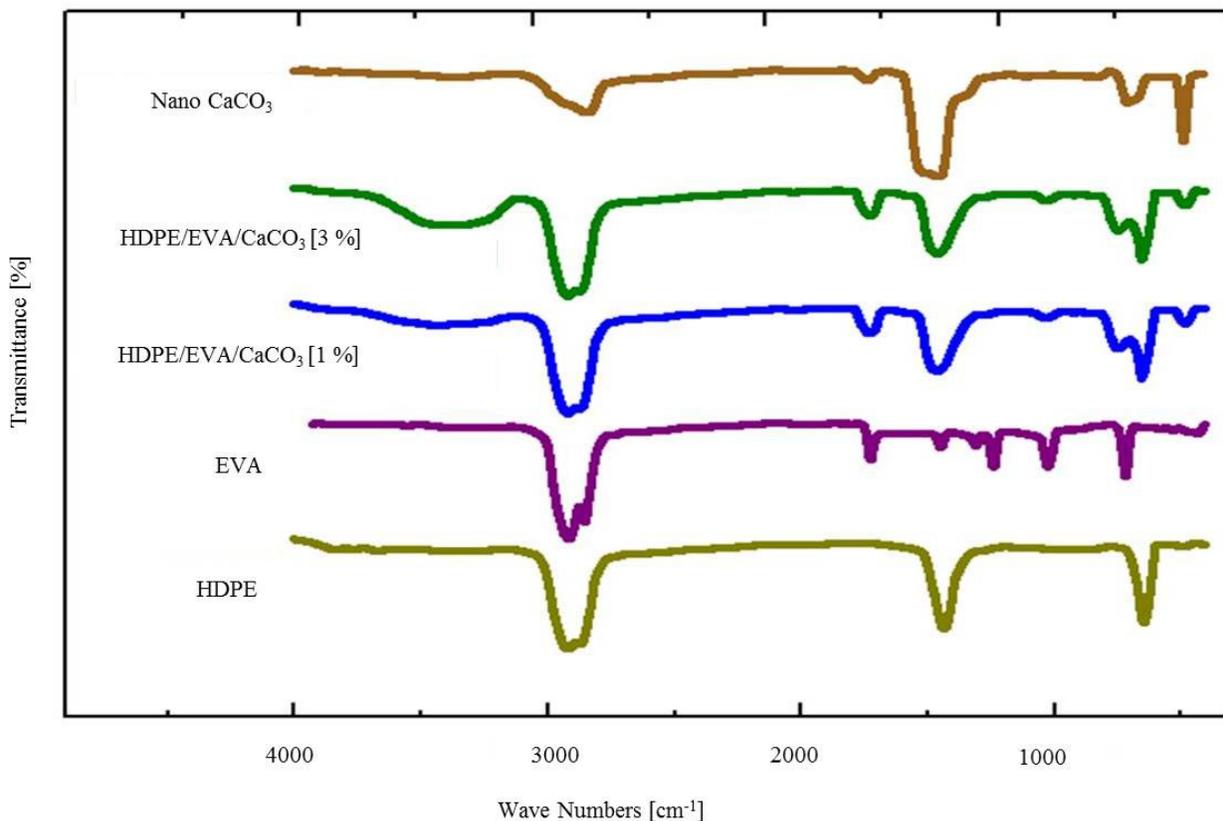
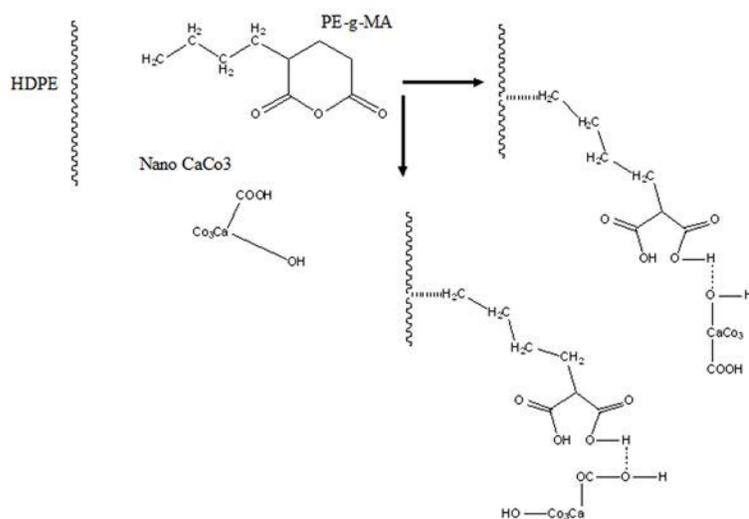


Figure-1
 FTIR spectra of pure HDPE, MA-g-PE, CaCO_3 , HDPE/MA-g-PE/ CaCO_3 nanocomposite



Scheme-1
 Schematic reaction of HDPE and MA-g-PE

Thermal degradation: Thermal degradation of nanocomposites was investigated by determining mass loss (heating rate 5 °C/min). Results of all samples were presented in figure-2. The weight loss (TG %) and mass derivative (DTG) curves of all nanocomposites compared with neat HDPE. As it can be seen in DTG figure, the maximum decomposition rates were increased with increase of CaCO₃ content. By comparing behavior of samples, it can be seen that all samples show different thermal degradation: HDPE showed degradation step in 461°C but while with addition of PE-g-MA to HDPE this point decreased to 456°C as compatibilizer have lower decomposition temperature. As shown in figure-2, PE-g-MA/HDPE blend have two decomposition steps. One is related to PE-g-MA degradation

temperature and the other is related to HDPE degradation temperature. By addition of nano particles, decomposition steps increased. Decomposition temperature of samples with compatibilizer was 471°C and without compatibilizer felt down to 469°C. This behavior was usual in nanocomposites with different nano particle that recorded in some literatures¹⁸⁻¹⁹.

The stabilization of samples with nano is related to the effect of particles in the evolution of formed gasses from polymer matrix⁴. In samples contained compatibilizer, the interaction between HDPE and CaCO₃ via PE-g-Ma caused thermal degradation point increment.

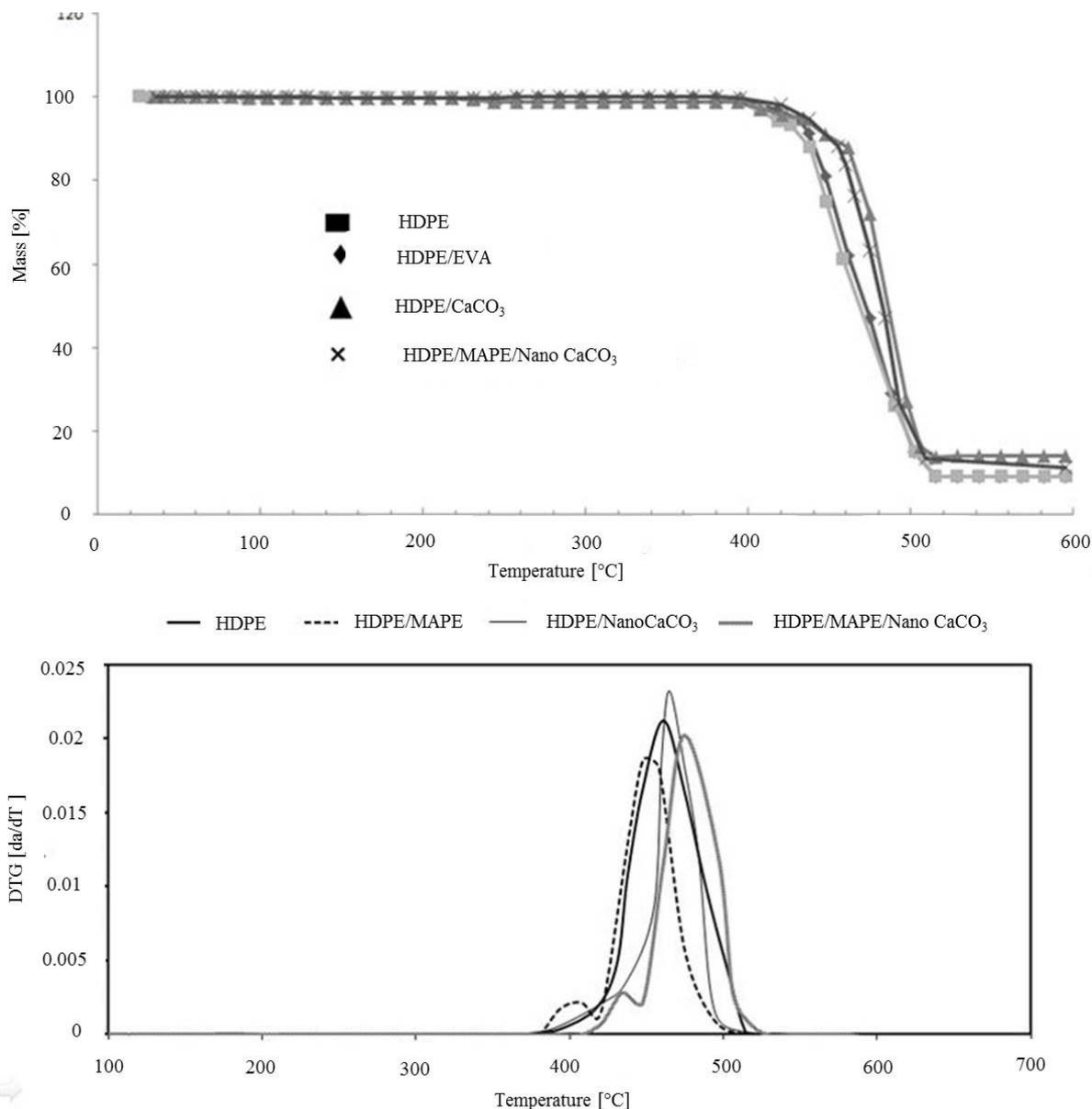


Figure-2
 The weight loss (TG %) and the derivative mass (DTG) curves of samples

The kinetic of Thermal decomposition: Thermal decomposition kinetic of HDPE/ CaCO₃ nanocomposites was investigated. As can be concluded from TGA and DTG curves, the maximum decomposition rate increased with addition of nano CaCO₃. For analyze exact thermal decomposition of nanocomposites, degradation mechanism of nanocomposites studied with different parameters like activation energy E, pre exponential factor A and overall reaction order n.

The activation energy, E, of thermal degradation calculated by model fitting and model free methods^{12,20}. All of kinetic analysis is characterized by the basic equation of conversion α for thermal decomposition (nitrogen atmosphere) as mentioned in equation-1:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

Where T is the temperature, α is the conversion, t is the time and f(α) is the reaction model. The reaction model could be different form that in this article is $(1 - \alpha)^n$ ⁵⁴. By the Arrhenius equation the kinetic equation is achieved by equation-2:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right)(1 - \alpha)^n \quad (2)$$

Where E is activation energy, A pre-exponential factor, n is overall reaction order and E is activation energy are the Arrhenius parameters and R is the gas constant. Our studied samples were heated at a constant rate that led to non-isothermal conditions. There are several relationships that can be used to compute Arrhenius parameters which gains from equation-3:

$$\frac{d\alpha}{dt} = \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right)(1 - \alpha)^n \quad (3)$$

Where $\beta = dT/dt$ is the heating rate.

Such approximation gives can be calculated by Kissinger²¹, Freeman-Carroll²² and other equations.

Figure-3 was shown TGA and DTG curves of HDPE/MAPE/nano CaCO₃ under nitrogen atmosphere at various heating rate such as 10, 15, 20 and 30 °C/min. Kinetic parameter were investigated only for HDPE with compatibilizer at higher content of nano CaCO₃ (3%).

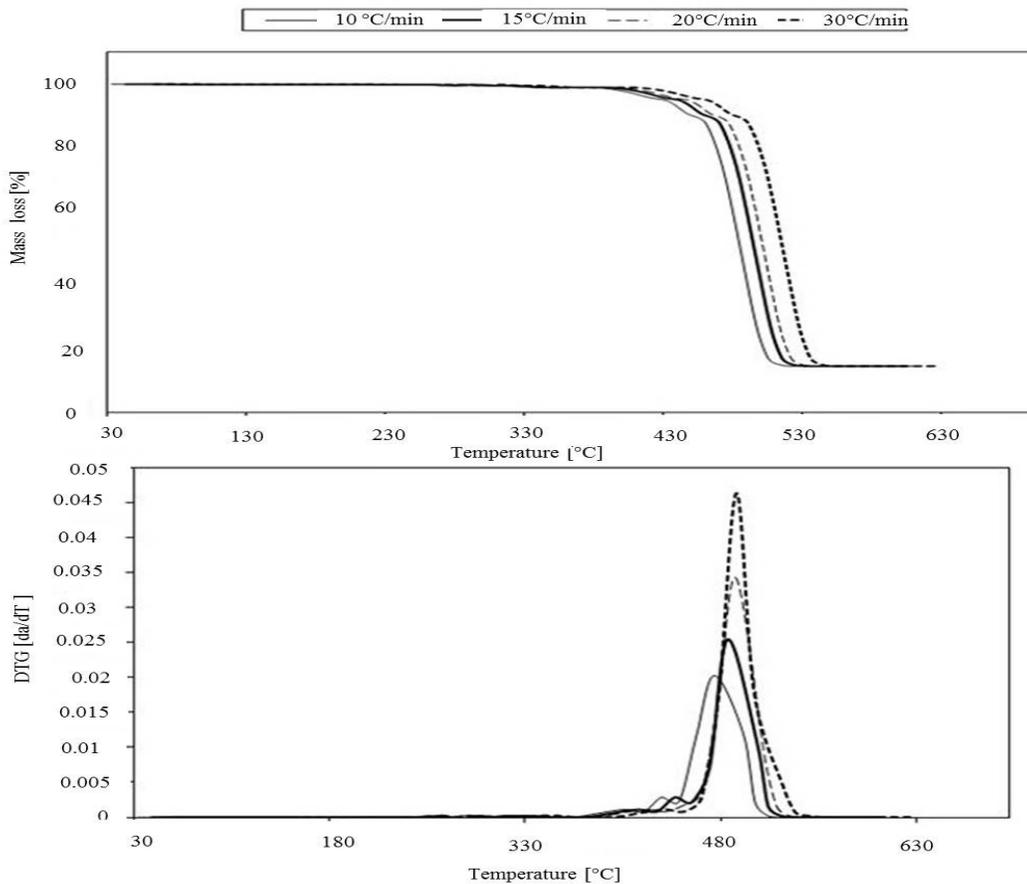


Figure-3
 TG and DTG curves of HDPE/MA-g-PE/nano CaCO₃ under nitrogen at various heating rate

It was found that curves moved to higher temperature with increasing the heating rate. In addition, as shown in figure-4 TGA and DTG curves of HDPE/MAPE under nitrogen atmosphere at same heating rate that used for nanocomposites and same condition was created. The plot of $1/T_{max}$ against $\ln \beta$ to calculate A_0 was shown in figure-5. The slope was equal to $-E/R$, thus the activation energy in max thermal degradation rate was obtained. As shown in figure-5 the slope for HDPE/MAPE/nano $CaCO_3$ was higher than samples without

nanoparticle. Activation energy of samples was increased with addition of nanoparticles in max thermal degradation rate as attendance of nanoparticles in polymer matrix, with reduction of gas formation in matrix and also interaction of nano particles and polymer chains. The value of A_0 was obtained from equation-3 with substituting value on the plots that drawing in figure-5. For computing activation energy and reaction order of HDPE/PE-g-MA blends with and without nanoparticles were used various methods that on the following explained.

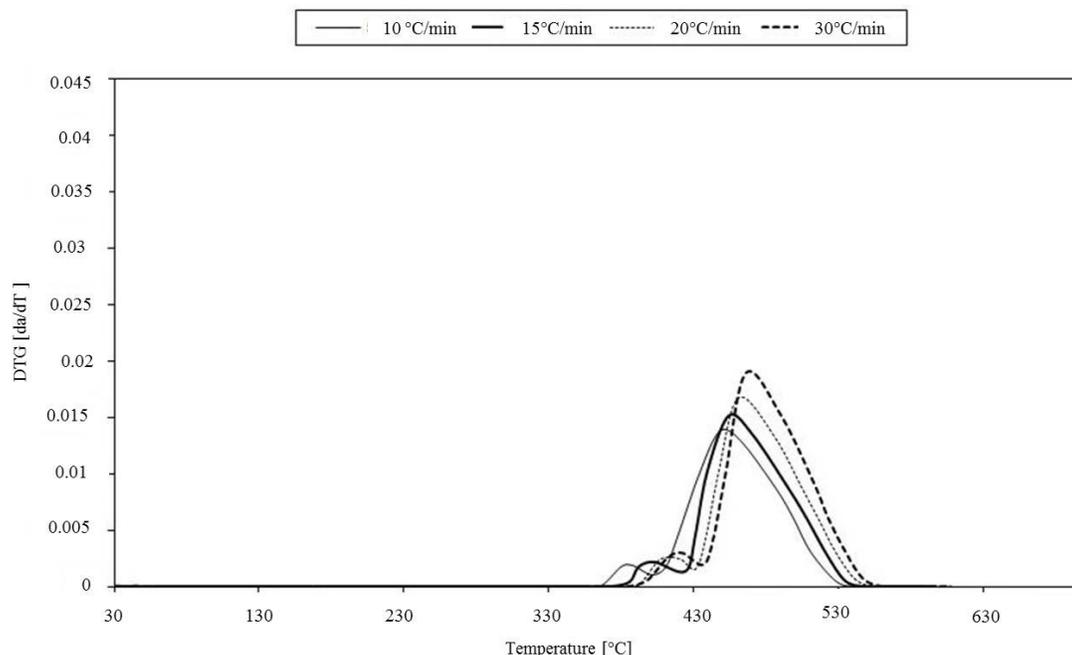


Figure-4
 TG and DTG curves of HDPE/MA-g-PE under N_2 gas at various heating rates

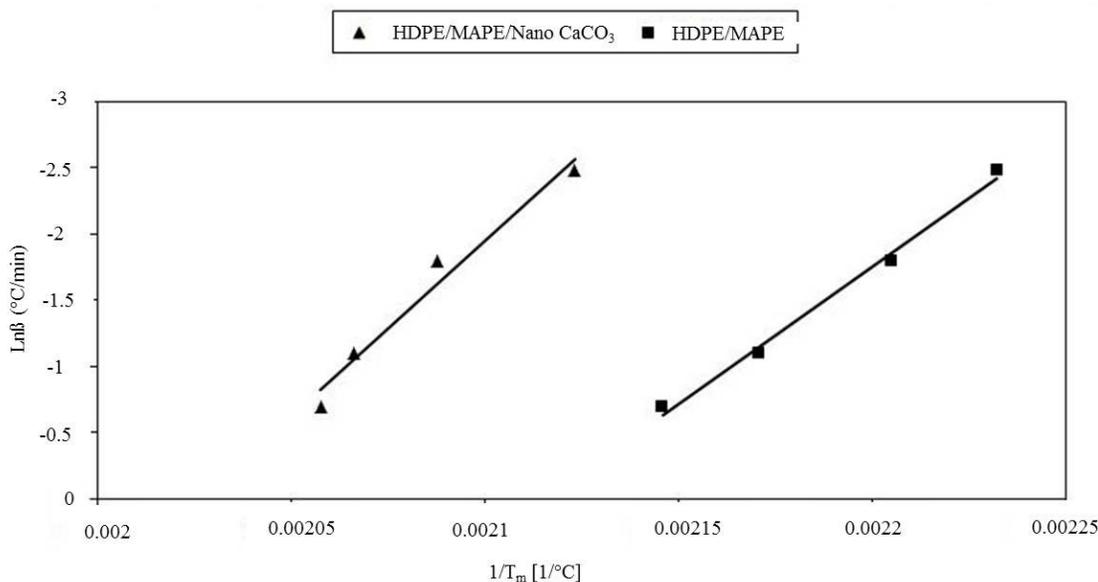


Figure-5
 $1/T_{max}$ against $\ln \beta$ plot for A_0 calculation

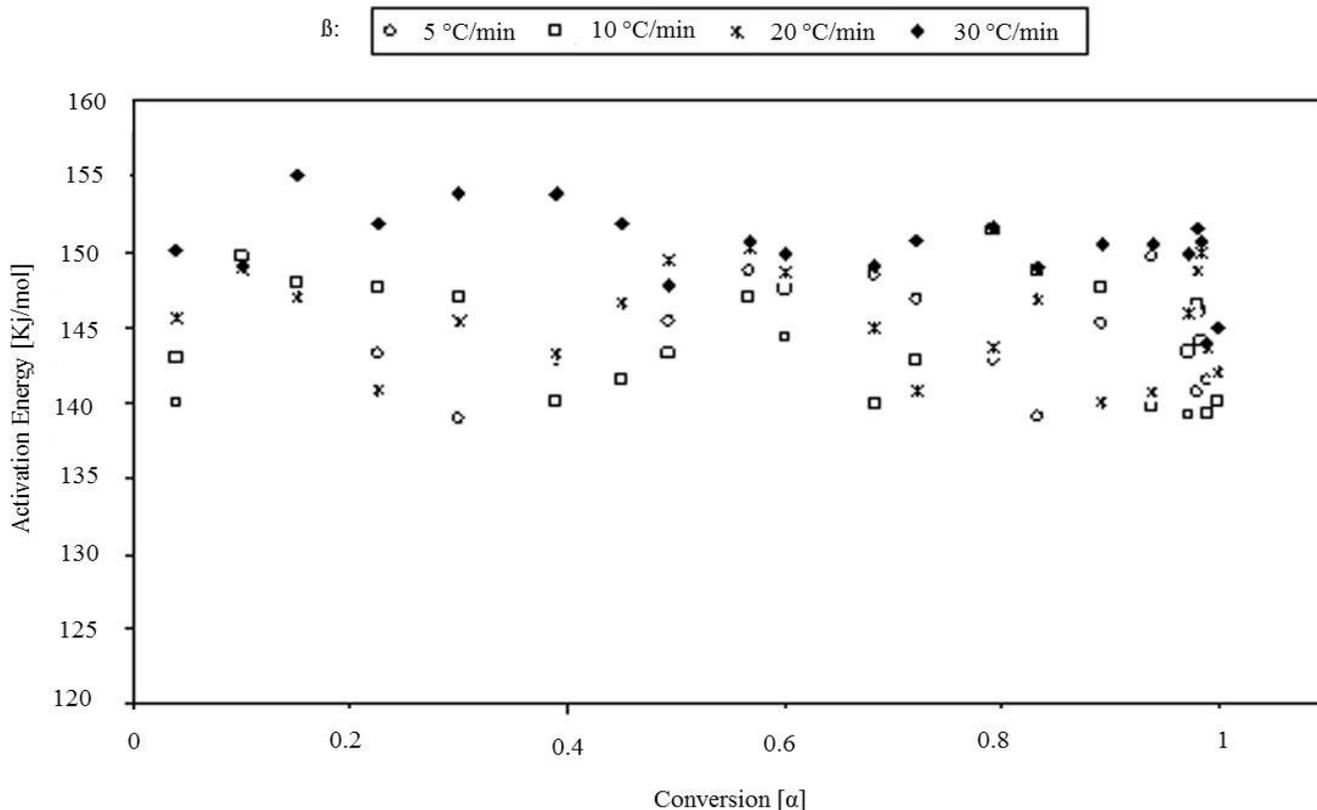


Figure-6
Activation energy calculated from TG data by numerical method

Dynamic Method: According to collision theory on $T^{0.5}$ in equation 3, A is not thoroughly constant^{19,26}. With substituting of $\beta=dT/dt$ the equation could be shown in equation 4:

$$\frac{d\alpha}{dT} = \frac{A_0}{\beta} \exp\left(\frac{-E}{RT}\right)(1-\alpha)^n T^{0.5} \quad (4)$$

By differentiation of equation 4 and replacement of E and n give the following expression for them:

$$E = -RT \ln \left[\frac{\left(\frac{d\alpha}{dt}\right)}{A_0 T^{0.5} (1-\alpha)^n} \right] \quad (5)$$

$$n = \frac{\left[\beta \left(\frac{d^2\alpha}{dT^2} \right) / \left(\frac{d\alpha}{dt} \right) - \frac{E}{RT^2} - \frac{0.5}{T} \right] (1-\alpha)}{\left(-\frac{d\alpha}{dT} \right)} \quad (6)$$

Kim and et al.¹⁹ at maximum degradation rate by setting $d^2\alpha/dT^2$ to zero reached to following equation that give from plot of $\ln\beta$ versus $1/T_m$.

$$\ln \beta = \ln A_0 + 1.5 \ln T_{\max} - \ln \left(\frac{E_{\max}}{RT_{\max}} + 0.5 \right) - \frac{E_{\max}}{RT_{\max}} \quad (7)$$

T_{\max} was maximum peak of samples that shown in DTG curves and E_{\max} was activation energy of samples at maximum degradation rate. The A_0 values obtained by equation 7 summarized in table-2. The related activation energy and reaction order obtained from A_0 , equation 5 and equation 6. The Values summarized in table-2. Activation energies and reaction order of nanocomposites are higher than that without nano. By comparison of all data's, as it can be seen, activation energy magnitudes of HDPE/MA-g-PE/nano CaCO_3 are higher than values of samples without nano fillers as a result of stabilization performance of CaCO_3 in thermal degradation of HDPE/MA-g-PE.

Table-2
Maximum activation and A_0 value in different heating rate

Heating rate β (°C/min)	Activation energy, E_m (kJ/mol)		Pre-exponential factor, A_0 (1/s.K ^{1/2})	
	With Nano	Without Nano	With Nano	Without Nano
5			$1.43 \cdot 10^{21}$	$5.57 \cdot 10^{16}$
10	334	165.2	$1.37 \cdot 10^{21}$	$5.41 \cdot 10^{16}$
20			$1.33 \cdot 10^{21}$	$5.02 \cdot 10^{16}$
30			$1.32 \cdot 10^{21}$	$5.05 \cdot 10^{16}$

Figure-5 was shown plots of $\ln\beta$ versus $1/T_m$ which calculated the factor A_0 in Equation-7. The slopes of straight lines that

drew in plot were $-E_{\max}/R$, so the activation energy in maximum thermal decomposition was obtained. The value of the A_0 and E_m were summarized in table-3. In dynamic model activation energy and overall order reaction were obtained from A_0 with substitution on Equation-5 and 6. Figure-6 was shown the activation energy from TG data by numerical method. Activation energy of samples with nano in different conversion has lower dispersion state than samples without nano particles. This issue can be caused by nano CaCO_3 on thermal degradation of nanocomposites with stabilized polymer chain in large temperature amplitude, so the result was shown the activation energy in single heating rate was only slightly variation in comparison samples without nano particles. Also the nanocomposites activation energy in different heating rates more dependent on rate of heating in comparison the samples without nano. Besides, with heating rate enhancement, the activation energy was increased. These results in $\beta = 30 \text{ }^\circ\text{C}/\text{min}$ was more evident.

According to table-2 and table-3, average of the activation energy in different heating rates was 329.3 kJ/mol and maximum of activation energy of nanocomposites that driven from slopes of plot $\ln\beta$ against $1/T_m$ was 334 kJ/mol, so there were nearly same. While for samples without nano particles this value was 165.2 and 148.72 kJ/mol. This difference may be caused by attendance of PE-g-MA in the blends.

Figure-7 illustrates dependence of the activation energy on degree of conversion (α) for HDPE/PE-g-MA and its nanocomposites. As it can be seen, all values of the activation energy of nanocomposites have higher values than HDPE/PE-g-MA. CaCO_3 has a stabilization effect on the polymeric matrix.

Effect of activation energy on degree of conversion: The effect of activation energy of degree of conversion is shown in figure-7. The values were divided into two regions. The first part is related to activation energy from $0 < \alpha < 0.63$ and the second part related to the values from $0.63 < \alpha < 1$. For nanocomposite samples, these values were decreased with conversion enhancement up to $\alpha=0.63$ and this slight reduction was linear, meanwhile the values of activation energy in the second region become a plateau. Enhancement of E values by increment of α is a typical phenomenon for many polymers. The same results were reported in several reports based on the multistep TG curve³⁰.

Besides we can conclude that E is dependent on α and the FWO method leads to close values of E . As shown in figure-7, E magnitudes sharply decreased down to $\alpha=0.63$ and show a peak increase at $\alpha=0.71$. Afterward we found a similar trend to the first part. We can conclude that addition of PE-g-MA to HDPE matrix, the decomposition temperature of composites was declined and subsequently division of activation energy versus conversion was irregular. These differences can be due to the approximation of the temperature integral which is used in derivations of the relations that were gained by the FWO method.

Addition of nano particles combined with PE-g-MA chains can motivate stabilized properties.

According to table-4, the values of the activation energy at different heating rates were higher than the activation energy for HDPE/PE-g-MA.

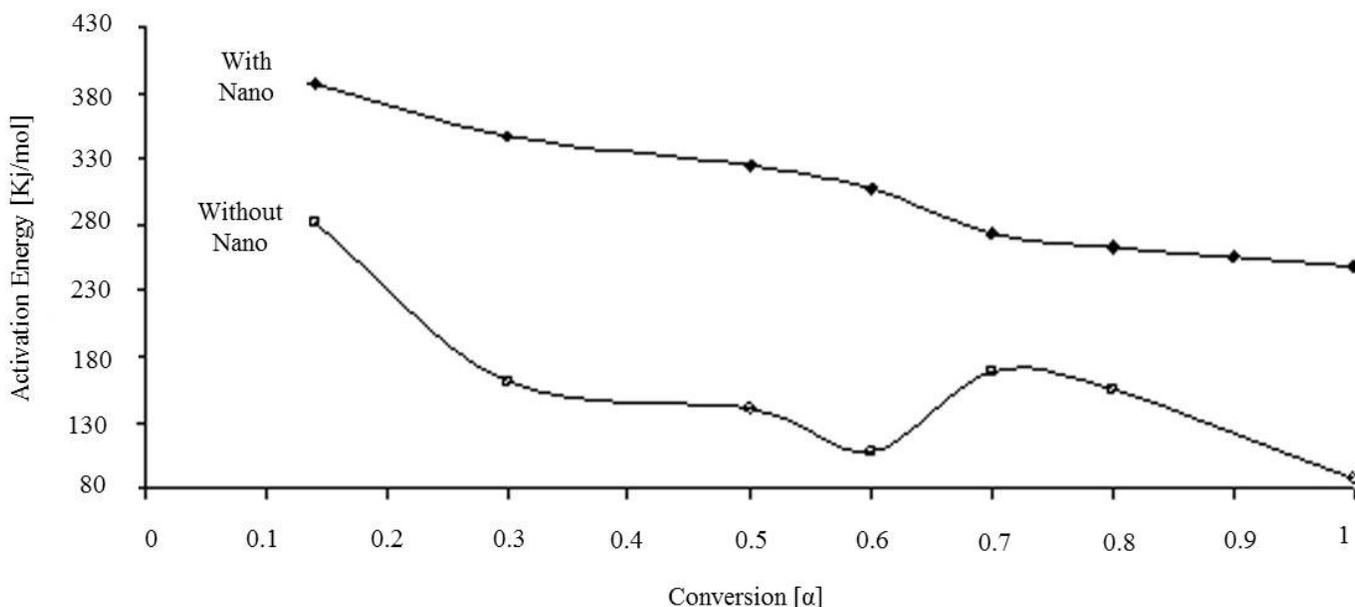


Figure-7

The dependence of the activation energy on the degree of conversion (α) for HDPE/MA-g-PE and its nanocomposite

Table-3
Activation energy and order reaction of samples with and without nano CaCO₃ in different heating rate

Heating rate β (°C/min)	Activation Energy, E		Order reaction, n	
	With nano	Without nano	With nano	Without nano
5	312.676	146.866	0.963	0.951
10	318.921	147.893	0.971	0.957
20	323.194	149.448	0.979	0.962
30	362.353	150.672	0.982	0.968

Table-4
Kinetic parameters obtained with different of analytical methods

Method		Heating Rate	Reaction order, n		Activation energy, E(kJ/mol)	
			With nano	Without nano	With nano	Without nano
Dynamic Method		5 °C/min	0.963	0.951	312.676	146.9
		10 °C/min	0.971	0.957	318.921	147.9
		20 °C/min	0.9791	0.962	323.194	149.5
		30 °C/min	0.9817	0.968	362.353	150.7
Model Fitting Methods	Freeman-Carroll	5 °C/min	1.1064	1.097	252.94	225.73
		10 °C/min	1.1203	1.103	287.56	243.54
		20 °C/min	1.1292	1.109	310.53	269.91
		30 °C/min	1.1475	1.118	360.46	282.52
	Flynn-Wall	5 °C/min	0.551	0.34	182.6	168.5
		10 °C/min	0.6	0.35	247.96	184
		20 °C/min	0.6	0.41	335.96	218.9
		30 °C/min	0.57	0.5	445	286
Model Free Methods	Friedman	5 °C/min	0.6332	0.637	177.5	161.6
		10 °C/min	0.623	0.674	185.3	150
		20 °C/min	0.6164	0.746	183.3	126.6
		30 °C/min	0.64	0.758	201.8	126.8
	Kissinger	-	1	1	205.9	165.2
	Ozawa	-	-	-	304.1	157.6

Figure-8 shows overall reaction order and activation energy against heating rates. As it shows, the reaction order and determined activation energy in all methods was greater than obtained values for sample without nano particles as they located inside the polymer chains and prevent the degradation of the sample.

The Kissinger method⁵⁸ can calculate without considering the difference of heating rates and calculated at maximum temperature of samples that obtained on DTG curves. Also the Flynn wall method was calculated at maximum temperature but by applying different heating rates. By applying several heating rates the values of activation energy and reactions order are more dependent to heating reaction. The E and n values which obtained from dynamic methods are more dependent to time and conversion. The data of these methods was more acceptable than other methods, as these methods were used time and conversion for E and n calculations. Ozawa-Flynn-Wall method was calculated only the activation energy in different conversions and their results were closed to dynamic methods.

The Freeman Carroll method is in contrary with Kim et al.¹² result that they claimed this method gave variety of results at various heating rates. E and n values of Freeman Carroll and Flynn Wall methods were affected by heating rates with similar trends (figure-9). Lines approximately similar and the slope of these lines were based on n and intercept of line was $-E/R$ Also the Friedman Carroll was calculated E and n from different conversion. According to Friedman research²⁴. We used the conversion values ranging from 0.43 to 0.91. Based on TGA curves on these conversions, samples experienced the thermal degradation. Figure-10 shows the values of $d\alpha/dt$ versus $1/T$ for several conversions ($0.43 < \alpha < 0.91$) and E values calculated from the slope $-E/R$. Also the reaction order values obtained from intercept of plots. The value which obtained from the intercept equal to $\ln[A(1-\alpha)^n]$ terms. This method had reliable results for nanocomposite and the value of E and n for nanocomposites were increased with increasing of heating rate continuously. We should consider that these conditions applicable just for samples without nanofillers.

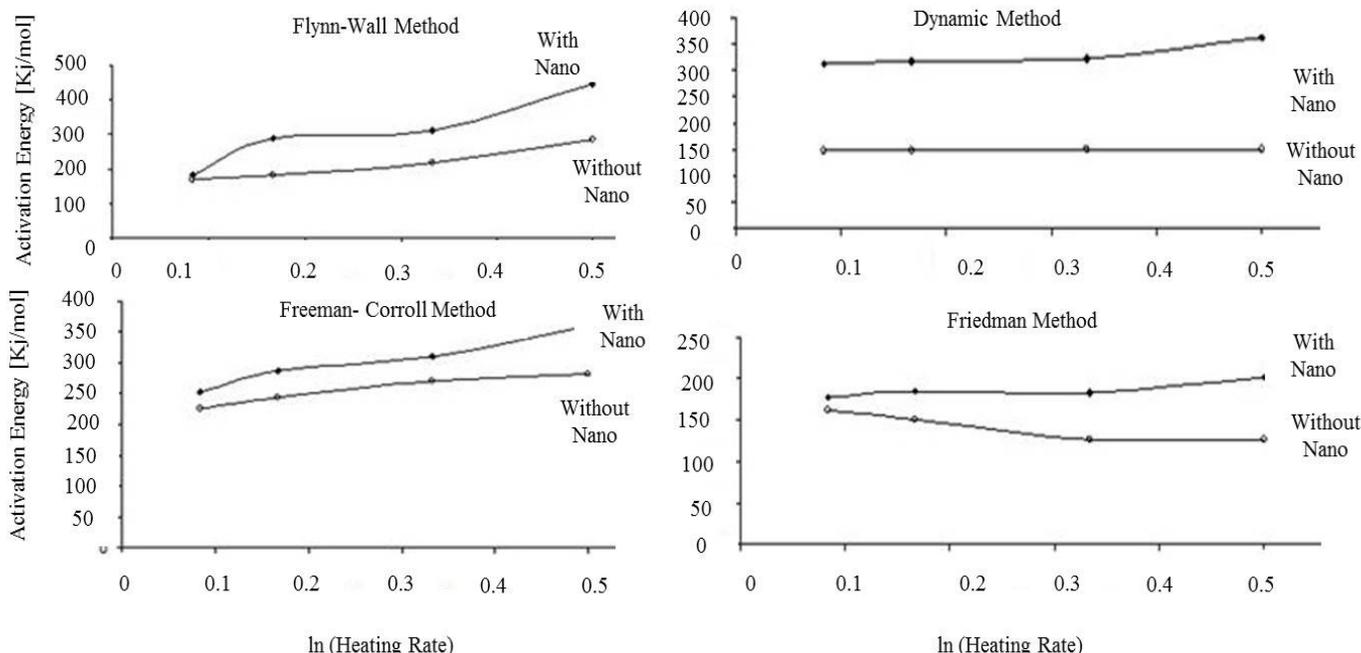


Figure-8
The activation energy and the overall reaction order against heating rates of samples

The degree of crystallinity of semi-crystalline polymers has a considerable effect on their DSC analysis. The enthalpy of fusion of HDPE/ PE-g-MA /nanoCaCO₃ nanocomposites used to calculate the crystallinity of nanocomposites. The crystallinity of samples can be calculated by equation-8:

$$X_c = \left\{ \frac{\Delta H_c}{(1 - \phi)\Delta H_m^0} \right\} \times 100\% \quad (8)$$

where X_c is crystallinity of samples, ΔH_c is the measured enthalpy of fusion of sample from DSC thermograms, Φ is the mass fraction of nano-CaCO₃ in sample, ΔH_m⁰ is a enthalpy of fusion of 100% crystalline HDPE (293 J g⁻¹)⁴⁰.

The results relating to the melting and crystallization temperatures and heat of fusion (ΔH_m) of the blends with different nano CaCO₃ content are summarized in table-5. CaCO₃ nano fillers had significant effect on the melting temperature of PE. Attendance of nano sized fillers led to increment the total crystallinity of the nanocomposites. These results have a good agreement with previous studies in HDPE nanocomposites which containing different amount of nanoparticles. Sahebian et al.²⁵ reported that nano-sized calcium carbonate in HDPE/CaCO₃ nanocomposites had a major effect on crystalline percentage, melting point and crystallization rates and heat of melting of HDPE. These types of behaviors were also, observed with attendance of nano sized SiO₂ and MMT where the crystallization rates in these nanocomposites are higher, compared to neat HDPE²⁶. In addition, it seems that not only nanoparticles can increase the crystallization rates of polymers²⁷, but also they may cause an increase on degree of

crystallinity. Shentu et al²⁸, Ujhelyiová et al²⁹ reported the polymers containing nano CaCO₃ and compatibilizer crystallized at a higher temperature as a result of dispersion enhancement of nanoparticles and increment of nucleation sites in the matrix.

Table-5
DSC analyzes results for nano composites

CaCO ₃ content wt %	HDPE/MA-g-PE/NanoCaCO ₃			
	T _m	T _c	H _c	X _c
0	130.3	118.75	152	51.87
1	130.76	118.98	153.1	52.775
3	131.45	120	154.5	54.3
5	132.65	120.87	153.4	54.97

Morphological properties: Morphological structure of samples studied by SEM and the results shows in figure-11. The samples which contained nano fillers, had smooth area after fracture meanwhile attendance of nanofillers led to rough surface. In order to improve distributive mixing of nano fillers, addition of coupling agent is essential. There are several methods in order to enhance the dispersion states of nano fillers in polyolefin base matrix. We used PE-g-MA as a compatibilizer between nanofiller and PE matrix. Introduction of PE-g-MA led to interaction of nano particle surface with HDPE as a matrix. As it shown in figure-12, dispersion of nano particles improved with attendance of PE-g-MA as coupling agent to some extent.

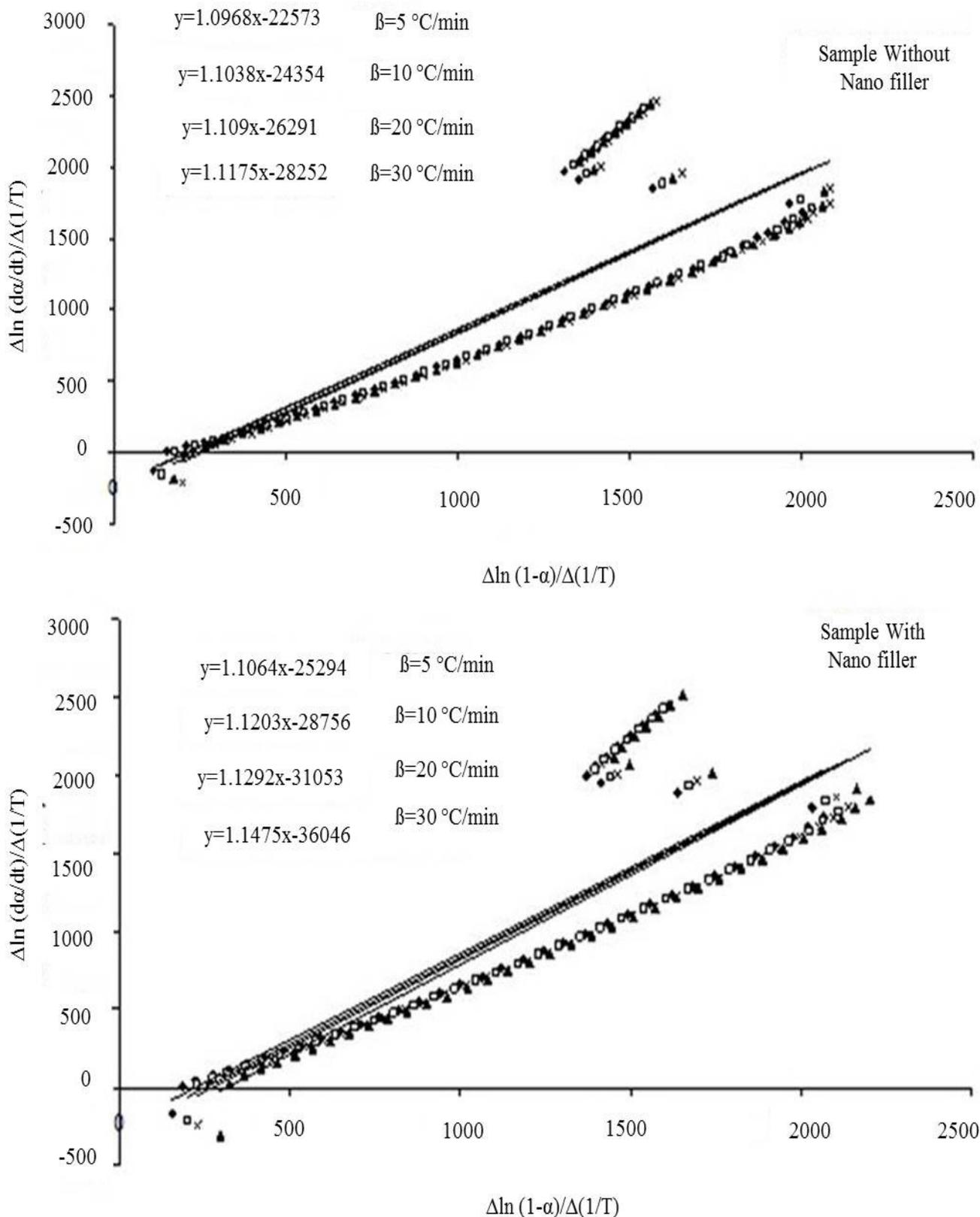


Figure-9
 The values of E and n of Freeman Carroll and Flynn Wall methods versus heating rates

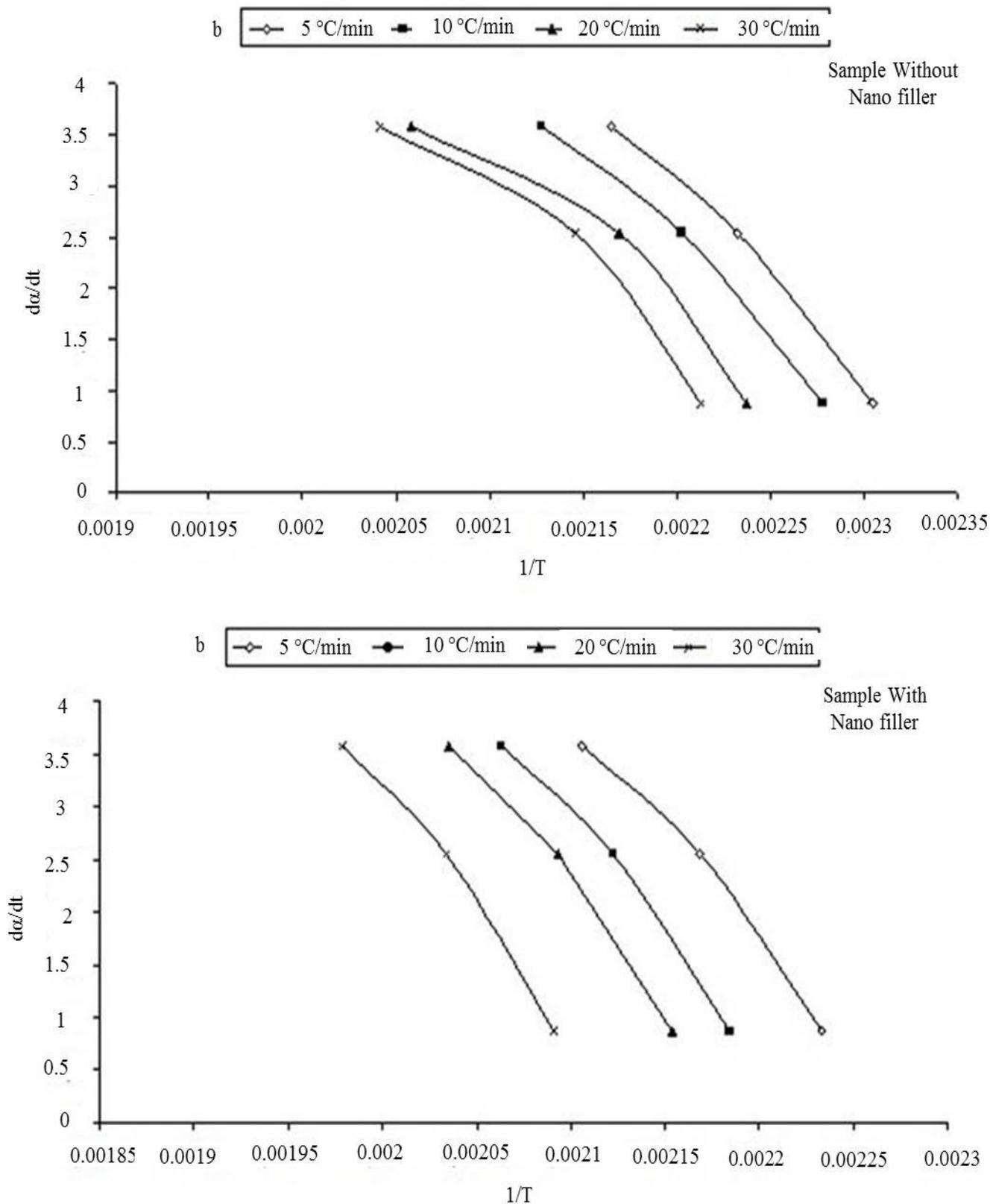


Figure-10
 The values of $d\alpha/dt$ versus $1/T$ at various conversions ($0.43 < \alpha < 0.91$)

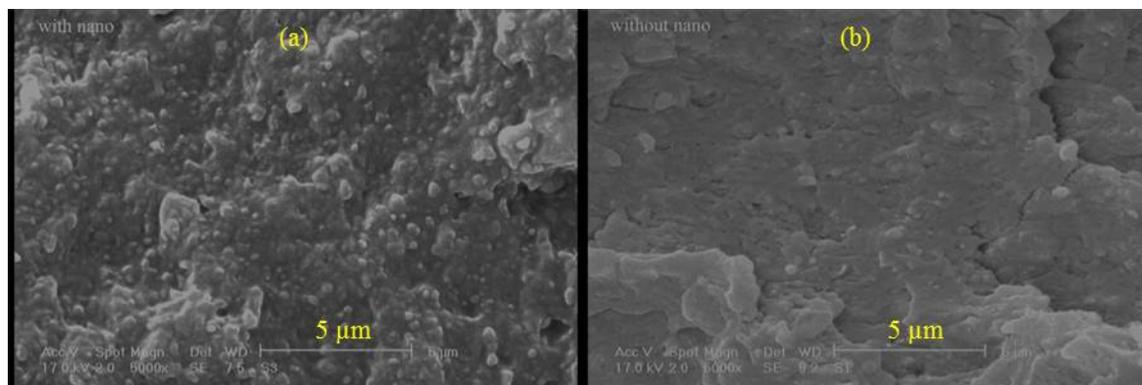


Figure-11
SEM micrographs of HDPE/MA-g-PE and HDPE/MA-g-PE/nanoCaCO₃ (3 wt%)

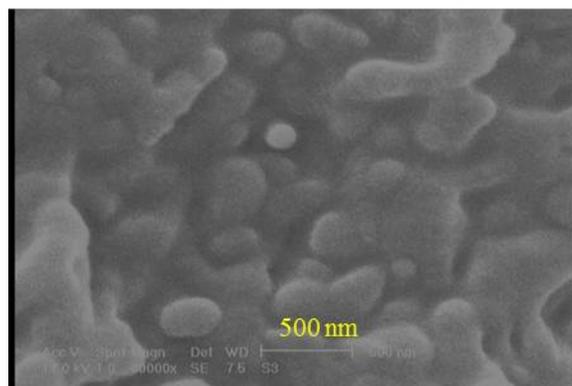


Figure-12
SEM micrograph of HDPE/MA-g-PE/nanoCaCO₃ (3 wt%)

Conclusion

Attendance of compatibilizer led to enhancement of CaCO₃ compatibility of these inorganic nanoparticles with PE matrix which it shown by FTIR spectra. With incorporation of MA-g-PE to HDPE the onset degradation temperature of blend decreased but with addition of MA-g-PE to nanocomposite the onset degradation temperature increased this as a result of adhesion between nano sized fillers and HDPE.. Kinetic degradation models were studied and all of these models were shown that the activation energy of nanocomposite was higher than its blend. The dynamic model results were more appropriate than other models. Nano sized CaCO₃ had significant effect on the melting temperature of PE and it increased the total crystallinity of the nanocomposites.

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