



A Kinetic Evaluation for PANSAs Doped Low Density Polyethylene Blends

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Abstract

In our previous study, we prepared blends of low density polyethylene (LDPE) with semiconductor polymer, poly (1-amino-2-hydroxynaphthalene-4-sulfonic acid) (PANSAs), in different mixing ratios. In that study, the findings on some physical and chemical properties of the blends prepared were also presented. In this study, it was aimed to investigate the thermal decomposition kinetics of these prepared blends. For this purpose, thermograms of PANSAs doped LDPE blends at four different heating rates were obtained. With the addition of PANSAs into LDPE, it was observed that the initial decomposition temperature and maximum decomposition temperature of LDPE increased. Thermal decomposition kinetics of blends were performed using the integral isoconversional methods (Kissinger, Kim-Park (KP), Tang, Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO)) in addition to differential isoconversional method (Friedman method). The activation energy values calculated by Kissinger, KP, Tang, KAS, FWO and Friedman methods and found to be 187.9, 200.2, 171.90, 171.78, 171.70 and 171.89 kJ mol⁻¹ for 0.5 % PANSAs doped LDPE, 193.9, 206.2, 173.31, 172.87, 172.98 and 172.78 kJ mol⁻¹ for 1 % PANSAs doped LDPE and 207.0, 219.2, 196.94, 197.09, 198.08 and 208.10 kJ mol⁻¹ for 0.5 % PANSAs doped LDPE, respectively. Thermal decomposition mechanism for blends was proposed with the help of master plot curves.

Keywords: Low density polyethylene, thermal decomposition kinetic, activation energy.

1. Introduction

Low density polyethylene is the one of the most produced and used thermoplastics in the plastics industry due to ease of production, low thermal conductivity and good chemical resistance. [1]. However, polymers are exposed to heat, light and mechanical influences during their daily use or production process. This causes deterioration in their physical and mechanical properties. To solve this problem, the various additives are used in the polymer formulations: antioxidants, UV, stabilizers, antistatic agents. In this way, it is aimed to extend the shelf life of the polymer [1]. Phenolic compounds are among the antioxidants commonly used to increase the thermo-oxidative resistance of polyethylene. Ascorbic acid, caffeic acid, curcumin, α -tocopherol and quercetin are some of the phenolic antioxidants used for this purpose.

[2]. Since this group of compounds has a low molar mass, it is difficult to miscible them with the polymers. The insertion of these compounds into polymer formulations also causes their decomposition or evaporation during polymer processing. [1,3]. These compounds may diffuse and accumulate on the polymer surface. One of the approaches used to solve this problem has been the use of high molar mass antioxidants. [2]. Recently, some polymeric antioxidants have been reported to be used effectively in polyethylene stabilization. Veronica Ambrogi et al. synthesized a phenolic polymer by oxidizing caffeic acid methyl ester with H₂O₂/HRP system. This polymer is reported to increase the thermo-oxidative and photo-oxidative resistance of LDPE [2]. Polyguaiacol is another phenolic polymer synthesized by enzymatic process [3]. This polymer has been reported to increase the resistance of polypropylene against to thermal-

oxidative degradation and to improve the mechanical properties of the polypropylene. Polypyrogallol acid is other phenol based polymeric antioxidant used for this purpose. [4]. It has been reported that the addition of polypyrogallol acid into polypropylene provides an improvement in onset oxidation temperature and oxidation induction time parameters. Oligo (4-methoxyphenol) is a steric hindered and phenolic compound having high molecular mass. [5]. This compound was also found to be an effective antioxidant in polyethylene stabilization.

In our previous study, we reported the synthesis and characterization of a conjugated phenolic polymer (PANSAs) [6]. We prepared blends of this functional polymer with low density polyethylene (PANSAs /polyethylene) [7] and the prepared blends were characterized by their physical and chemical aspects. Here, it is aimed to study the thermal decomposition kinetics of the prepared blends. For this purpose, TG / DTG-DTA thermograms of the blends prepared were taken at different heating rates. The thermal solid state decomposition kinetics of PANSAs / polyethylene blends were evaluated by Kissinger, KP, Tang, KAS, FWO and FR methods.

2. Materials and Methods

2.1. Material

2.1.1. The preparation of PANSAs and PANSAs-LDPE blends

PANSAs was prepared by the oxidative polymerization of the ANSA as given in the literature [6]. Then, PANSAs's blends with LDPE (supplied from İzmir Aliağa refinery, sample code:F00556) in 3 different mixing ratios were prepared with the help of a micro extruder and the characterization of the prepared blends was presented in the previous study (Figure 1) [7].

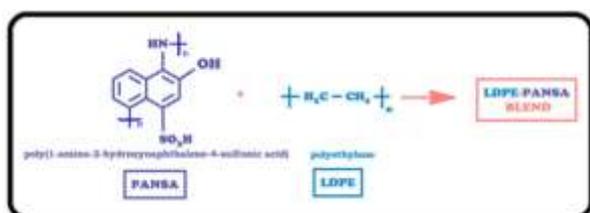


Figure 1. Synthesis of PANSAs/LDPE blends.

In this study, virgine LDPE, 0.5, 1 and 3% PANSAs doped LDPE were coded as AP₀, AP_{0.5}, AP₁ and AP₃, respectively.

2.2. Method

2.2.1. Thermal analysis

Thermal analyzes of the blends were conducted by TG/DTG-DTA measurements. The analyzes were

followed with 8-10 mg samples in platinum vessels. Analyzes were performed under nitrogen gas at a flow rate of 100 mL min⁻¹ and the samples heated up to 1000 °C. Heating rates were selected as 5, 10, 15 and 20 °C min⁻¹. For a detailed kinetic analysis, all analyzes were repeated until reproducible results were obtained. Al₂O₃ was used as the reference material in the analyzes.

2.2.2. Kinetic Equations and Triplets (E, n, g(α))

There are many techniques using different approximations to calculate solid state decomposition kinetics. In this study, integral and differential isoconversional methods were used in the kinetics calculations of PANSAs/polyethylene blends. The mathematical equations related to these methods are given in below.

2.2.3. Kissinger Method

Activation energy can be calculated by using the following equation with Kissinger method without knowing the solid state decomposition reaction mechanism [8].

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = \left\{ \frac{AR}{E} + \ln\left[\ln(1 - \alpha_{\max})^{n-1}\right] \right\} - \frac{E}{RT_{\max}} \quad (2.1)$$

where β; heating rate, T_{max}; the temperature of the maximum reaction rate, A; pre-exponential factor, α_{max}; the maximum conversion fraction and n is the reaction order. A straight line is obtained from the graph of ln(β/T_{max}²) versus 1000/T_{max}. Activation energy can be calculated from the slope of this line.

2.2.4. Kim-Park Method

The thermal decomposition kinetics equation proposed by Kim-Park [9] is given as follows.

$$\ln \beta = \ln A + \ln\left(\frac{E}{R}\right) + \ln\left[1 - n + \frac{n}{0.994}\right] - 5.3305 - 1.0516\left(\frac{E}{RT_{\max}}\right) \quad (2.2)$$

Activation energy from the slope can be found according to the equation above.

2.2.5. Tang Method

Tang et al. proposed the following mathematical expression for the solution of the equation obtained from the Arrhenius parameter [10].

$$\ln\left(\frac{g(\alpha)}{T^{1.894661}}\right) = \left[\ln \frac{AR}{Rg(\alpha)} + 3.635041 - 1.894661 \ln E \right] - \left(\frac{1.001450E}{RT} \right) \quad (2.3)$$

At different heating rates, activation energy can be obtained from the slopes of the Arrhenius plots calculated for the same conversion values.



2.2.6. Kissinger-Akahira-Sunose Method

This method is an integral isoconversional method and the calculation of activation energy is done in similar ways as in other methods [8,11]. According to the Kissinger-Akahira-Sunose method, an equation is obtained as follows.

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left[\frac{AR}{Eg(\alpha)}\right] - \frac{E}{RT} \quad (2.4)$$

2.2.7. Flynn-Wall-Ozawa Method

This method is an integral method. In this technique, both A, f(α), E and temperature are independent of the conversion fraction. This technique uses the following logarithmic equation [12,13].

$$\log \beta = \log\left[\frac{AE}{R}\right] - \log \beta + \log p\left(\frac{E}{RT}\right) \frac{E}{RT} \quad (2.5)$$

When the Doyle approximation is used assuming E/RT > 20 for the integral function, the above equation can be simplified as follows.

$$\log \beta = \log\left[\frac{AE}{R}\right] - \log g(g(\alpha)) - 2.315 - 0.4567 \frac{E}{RT} \quad (2.6)$$

2.2.8. Friedman Method

The Friedman method uses the following equation based on the Arrhenius equation for thermal decomposition kinetics [14].

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(A) + n \ln(1 - \alpha) - \frac{E}{RT} \quad (2.7)$$

Here α, is the transformation in t time. R is the gas constant and T is the absolute temperature. A line is obtained by plotting 1/T versus ln (dα/dt) and E/R is determined from the slope of this line. In the above equations, α, g(α), β, Tm, E, A, R are respectively reaction degree, integral function of the transformation, heating rate, DTG peak temperature, pre-exponential factor and gas constant.

2.2.9. Determination of Kinetic Model by Master Plot Curves

When α = 0.5 is taken as the reference point, the following expression can be obtained according to the Arrhenius equation.

$$g(\alpha) = \left(\frac{AE}{\beta R}\right) p(u_{0.5}) \quad (2.8)$$

When u_{0.5} is taken as E/RT, the following equation is obtained.

$$\frac{g(\alpha)}{g(0.5)} = \frac{p(u)}{p(u_{0.5})} \quad (2.9)$$

The graphs of g(α)/g(0.5) versus α correspond to the theoretical master curves of the g(α) functions given in Table 1. Using an approximate formula P(u) = exp(-u)/[u(1.00198882u+1.87391198)] for P(u), a graph of P(u)/P(u_{0.5}) versus α at different heating rates can be obtained [15,16].

3. Results and Discussion

One of the most important parameters for the application of polymeric materials in industrial areas is their thermal stability. For this purpose, polymeric materials are exposed to heat and mass changes are examined.

The solid state decomposition kinetics of PANSA doped LDPE blends were investigated by TG-DTG-DTA thermograms. The each of curves were recorded for different heating rates (5, 10, 15, and 20 °C min⁻¹) (Figure 1). The TG-DTG and DTA curves of all AP_n blends showed that degradation occurs mainly in one step. In addition, it was found that the curves obtained were similar in character. Temperature values corresponding to the highest decomposition rate were determined from DTG curves and found to be 447, 456, 465 and 475 for AP_{0.5}, 448, 461, 466 and 476 °C for AP₁ and 456, 465, 469 and 476 °C for AP₃, respectively. As can be seen here, the curves are shifting to higher temperature values with increasing heating rate. Furthermore, the heating rates were selected at 5 °C min⁻¹ intervals to avoid overlapping the curves corresponding to the highest decomposition rate. The analyses were repeated until all curves were obtained with the same character.

Firstly, Kissinger and Kim-Park method, independent of the reaction mechanism, was used to calculate the kinetic parameters of the thermal decomposition of blends. Activation energy values for the solid state decomposition kinetics were 187.9 and 200.2 kJ mol⁻¹ for the AP_{0.5}, 193.9 and 206.2 kJ mol⁻¹ for the AP₁ and 207.0 and 219.2 kJ mol⁻¹ for the AP₃ according to the Kissinger and Kim-Park method, respectively. In Figure 2, Kissinger and Kim-Park curves obtained from experimental data for AP_n blends are given.

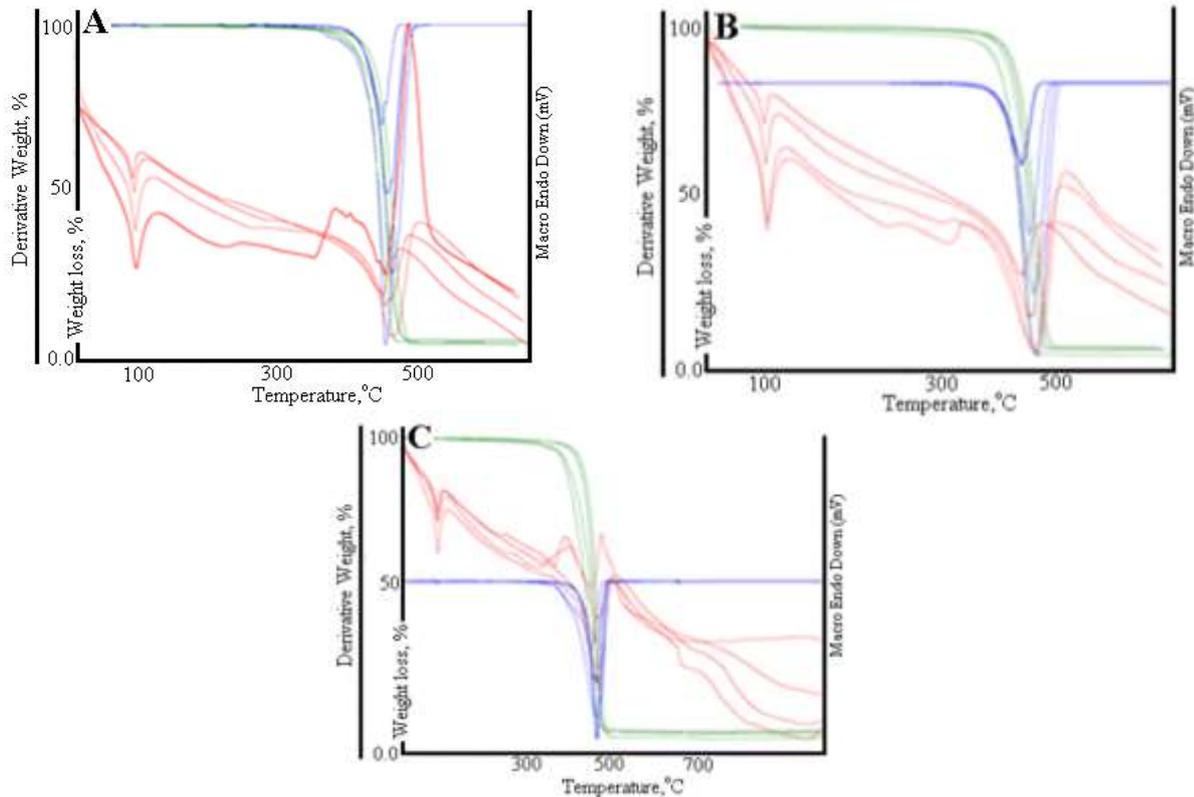


Figure 1. Typical dynamic TG / DTG and DTA thermograms recorded at different heating rates for AP_{0.5} (a), AP₁ (b) and AP₃ (c).

Table 1. Mathematical expressions used in solid state decomposition processes [17].

No	Mechanism	Symbol	Differential form, f(α)	Integral form, g(α)
Sigmoidal curves				
1	N and G (n=1)	A ₁	(1 - α)	[-ln(1 - α)]
2	N and G (n=1.5)	A _{1.5}	(3/2)(1 - α)[-ln(1 - α)] ^{1/3}	[-ln(1 - α)] ^{2/3}
3	N and G (n=2)	A ₂	2(1 - α)[-ln(1 - α)] ^{1/2}	[-ln(1 - α)] ^{1/2}
4	N and G (n=3)	A ₃	3(1 - α)[-ln(1 - α)] ^{2/3}	[-ln(1 - α)] ^{1/3}
5	N and G (n=4)	A ₄	4(1 - α)[-ln(1 - α)] ^{3/4}	[-ln(1 - α)] ^{1/4}
Deceleration curves				
6	Diffusion, 1D	D ₁	1/(2 α)	α ²
7	Diffusion, 2D	D ₂	1/(ln(1 - α))	(1 - α)ln(1 - α) + α
8	Diffusion, 3D	D ₃	1.5/[(1 - α) ^{-1/3} - 1]	(1 - 2α/3) - (1 - α) ^{2/3}
9	Diffusion, 3D	D ₄	[1.5(1 - α) ^{2/3}][1 - (1 - α) ^{1/3}] ⁻¹	[1 - (1 - α) ^{1/3}] ²
10	Diffusion, 3D	D ₅	(3/2)(1 + α) ^{2/3} [(1 + α) ^{1/3} - 1] ⁻¹	[(1 + α) ^{1/3} - 1] ²
11	Diffusion, 3D	D ₆	(3/2)(1 - α) ^{4/3} [[1/(1 - α) ^{1/3} - 1] ⁻¹	[[1/(1 - α) ^{1/3} - 1] ²
12	Contracted geometry shape (cylindrical symmetry)	R ₂	3(1 - α) ^{2/3}	1 - (1 - α) ^{1/3}
13	Contracted geometry shape (sphere symmetry)	R ₃	3(1 - α) ^{2/3}	1 - (1 - α) ^{1/3}
Acceleration curves				
14	Mamplé power law	P ₁	1	A
15	Mamplé power law (n=2)	P ₂	2α ^{1/2}	α ^{1/2}
16	Mamplé power law (n=3)	P ₃	(1.5)α ^{2/3}	α ^{1/3}
17	Mamplé power law (n=4)	P ₄	4α ^{3/4}	α ^{1/4}
18	Mamplé power law (n=2/3)	P _{3/2}	2/3(α) ^{-1/2}	α ^{3/2}
19	Mamplé power law (n=3/2)	P _{2/3}	3/2(α) ^{1/3}	α ^{2/3}
20	Mamplé power law (n=4/3)	P _{3/4}	4/3(α) ^{-1/3}	α ^{3/4}

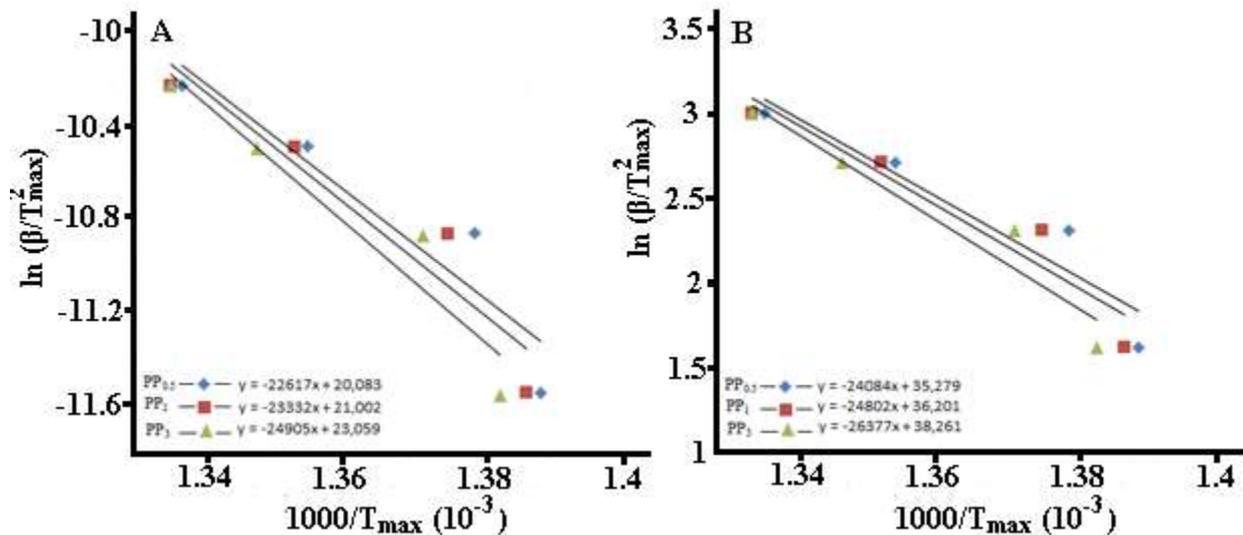


Figure 2. Kissinger (a) and Kim-Park (b) curves obtained from experimental data for AP_{0.5}, AP₁ and AP₃ blends for different heating rates.

Activation energy according to the Tang method can be calculated from the graph $\ln(\beta/T^{1.894661})$ versus $1000/T$. The average activation energies of the decomposition step for AP_{0.5}, AP₁ and AP₃ were found to be 171.90, 173.31 and 196.94 kJ mol⁻¹, respectively. Another method used in this study is the KAS method. Activation energy is calculated from the slopes of the graph of $\ln(\beta/T^2)$ versus $1000/T$, for conversion values $\alpha = 0.05-0.95$. The activation energies were calculated as 171.78, 172.87 and 197.09 kJ mol⁻¹ for the decomposition of AP_{0.5}, AP₁ and AP₃, respectively. These results were found to be very close to the values obtained by Tang method. Another method used in this study is FWO. At constant conversion values, the slope of the lines obtained from the $\log \beta$ versus $1000/T$ graph equals to $0.456E/RT$. From here, the activation energies can be found. The average activation energy values for AP_{0.5}, AP₁ and AP₃ were 171.70, 172.98 and 198.08 kJ.mol⁻¹, respectively. Finally, Friedman method, a differential method, was used. Activation energies were calculated as 171.89, 172.78 and 208.10 kJ mol⁻¹ for AP_{0.5}, AP₁ and AP₃.

As a result, the activation energy values of the solid state decomposition kinetics of AP_n blends were determined by Kissinger, Kim-Park, Tang, KAS, FWO and Friedman methods and found to be 187.9, 200.2, 171.90, 171.78, 171.70 and 171.89 kJ mol⁻¹ for AP_{0.5}, 193.9, 206.2, 173.31, 172.87, 172.98 and 172.78 kJ mol⁻¹ for AP₁ and 207.0, 219.2, 196.94, 197.09, 198.08 and 208.10 kJ mol⁻¹ for AP₃, respectively.

The changes of activation energies obtained by different methods for each blend corresponding to the conversion fraction are given in Tables 2,3 and 4. According to Table 2, Arrhenius type curves showing mass losses between $\alpha = 0.05-0.95$, it is seen that 130,32 kJ mol⁻¹

energy is required for the initial decomposition step of AP_{0.5}. The activation energies required for the decomposition step of the AP_{0.5} are very close to each other within the limits of $0.2 < \alpha < 0.8$. When the mass loss reaches 90%, an energy of 185.11 kJ mol⁻¹ of the first thermal decomposition step is required.

Table 2. Activation energies according to KAS, FWO, Tang and FR methods for solid state decomposition step of AP_{0.5}.

α	E_{Tang}	E_{KAS}	E_{FWO}	E_{FR}
0.05	131.12	130.32	131.31	132.22
0.1	146.25	145.71	145.52	145.58
0.2	174.63	174.32	173.85	175.33
0.3	176.32	175.16	176.03	176.29
0.4	176.78	177.52	176.78	176.63
0.5	176.17	175.74	176.35	176.73
0.6	176.45	177.54	175.51	176.03
0.7	175.62	176.24	176.21	176.02
0.8	179.47	177.74	178.12	180.27
0.9	184.06	183.13	185.11	183.62
0.95	194.09	196.23	193.96	192.11
Average	171.90	171.78	171.70	171.89

α , conversion degree; E , in kJ mol⁻¹

According to Table 3, Arrhenius type curves showing mass losses between $\alpha = 0.05-0.95$, it is seen that 130.03 kJ mol⁻¹ energy is required for the initial decomposition step of AP₁. The activation energies required for the decomposition step of the AP₁ are very close to each other within the limits of $0.2 < \alpha < 0.8$. When the mass loss reaches 90%, an energy of 188.76 kJ mol⁻¹ of the first thermal decomposition step is required.

Table 3. Activation energies according to KAS, FWO, Tang and FR methods for solid state decomposition step of AP₁.

α	E_{Tang}	E_{KAS}	E_{FWO}	E_{FR}
0.05	130.69	131.12	130.41	130.03
0.1	145.85	144.18	145.02	144.31
0.2	177.74	177.47	177.72	177.45
0.3	176.25	176.53	176.05	176.91
0.4	177.21	177.32	177.27	177.23
0.5	177.71	177.29	177.91	177.41
0.6	177.23	177.78	177.47	177.11
0.7	176.12	176.02	176.01	175.93
0.8	180.71	181.73	181.09	181.16
0.9	188.76	186.12	185.89	185.52
0.95	198.19	196.01	197.96	197.52
Average	173.31	172.87	172.98	172.78

α , conversion degree; E , in kJ mol^{-1}

According to Table 4, Arrhenius type curves showing mass losses between $\alpha = 0.05-0.95$, it is seen that $169.783 \text{ kJ mol}^{-1}$ energy is required for the initial decomposition step of AP₃. The activation energies required for the decomposition step of the AP₃ are very close to each other within the limits of $0.2 < \alpha < 0.8$. When the mass loss reaches 90%, an energy of $216.77 \text{ kJ mol}^{-1}$ of the first thermal decomposition step is required.

Table 4. Activation energies according to KAS, FWO, Tang and FR methods for solid state decomposition step of AP₃.

α	E_{Tang}	E_{KAS}	E_{FWO}	E_{FR}
0.05	169.78	171.66	171.66	179.78
0.1	180.74	181.21	182.33	191.21
0.2	201.31	201.69	202.47	209.22
0.3	200.33	200.37	201.36	210.66
0.4	200.35	200.11	201.89	210.87
0.5	200.78	201.33	201.01	210.63
0.6	200.37	199.96	202.54	210.14
0.7	200.87	200.74	202.31	210.89
0.8	200.77	200.12	202.77	210.09
0.9	205.38	204.87	203.11	216.77
0.95	205.71	206.03	207.44	228.91
Average	196.94	197.09	198.08	208.10

α , conversion degree; E , in kJ mol^{-1}

In Table 5, the activation energy values obtained by using various kinetic methods for AP_n blends are presented. In addition, it was found that the decomposition functions of AP_n blends (for $\alpha = 0.02-$

0.08 conversion values) can be expressed in a single mathematical equation as examined the changes of activation energies obtained by FWO, KAS, Tang and Friedman methods.

Table 5. Activation energy values of solid state decomposition kinetics of AP_n blends.

Blend	α	E_{Tang}	E_{KAS}	E_{FWO}	$E_{Friedman}$
AP _{0.5}	0.05-0.95	71.90	171.78	171.70	171.89
AP ₁	0.05-0.95	73.31	172.87	172.98	172.78
AP ₃	0.05-0.90	96.94	197.09	198.08	208.10

α , conversion degree; E , in kJ mol^{-1}

The solid state thermal decomposition mechanisms of the blends were examined by using the master plot curves (Figure 3).

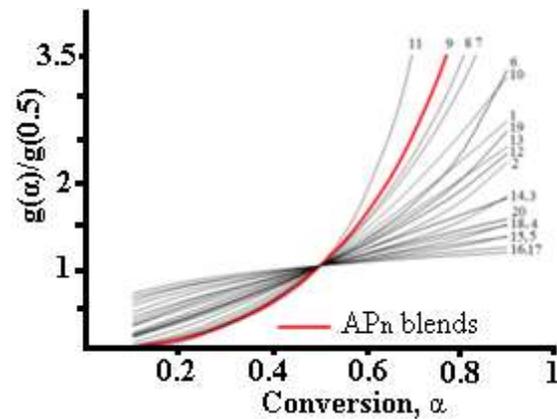


Figure 3. Master plot curves for AP_n blends.

The D₄ model (rate equation for diffusion reaction: $[1 - (1-\alpha)^{1/3}]^2$) was found to be the most suitable decomposition function for the thermal decomposition reaction of AP_n blends. In addition, all blends exhibited decollation type curves. These results are consistent with the results of other studies in the literature [18-20].

4. Conclusion

In here, the results of the kinetic analysis of PANSALDPE blends are presented. For this, thermal decomposition of the blends prepared in the previous studies at four different heating rates. Multiple heating rate based methods were used to evaluate the solid state decomposition kinetic of each blend. It was determined that the kinetic activation energy values obtained by different methods were close to each other. The activation energy values obtained for the blends are quite compatible with various polyethylene blends available in the literature [21]. The decomposition mechanism for the blends was also determined with the help of master curves and the D₄ model (rate equation for diffusion reaction: $[1 - (1-\alpha)^{1/3}]^2$) was found.



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Ethics

There are no ethical issues after the publication of this manuscript.

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