

## MIT Open Access Articles

*Kinetic Study on Thermal Degradation  
of Crosslinked Polyethylene Cable Waste*

The MIT Faculty has made this article openly available. **Please share** how this access benefits you. Your story matters.

**Citation:** Journal of Polymer Research. 2022 Jun 23;29(7):289

**As Published:** <https://doi.org/10.1007/s10965-022-03101-7>

**Publisher:** Springer Netherlands

**Persistent URL:** <https://hdl.handle.net/1721.1/143558>

**Version:** Author's final manuscript: final author's manuscript post peer review, without publisher's formatting or copy editing

**Terms of Use:** Article is made available in accordance with the publisher's policy and may be subject to US copyright law. Please refer to the publisher's site for terms of use.



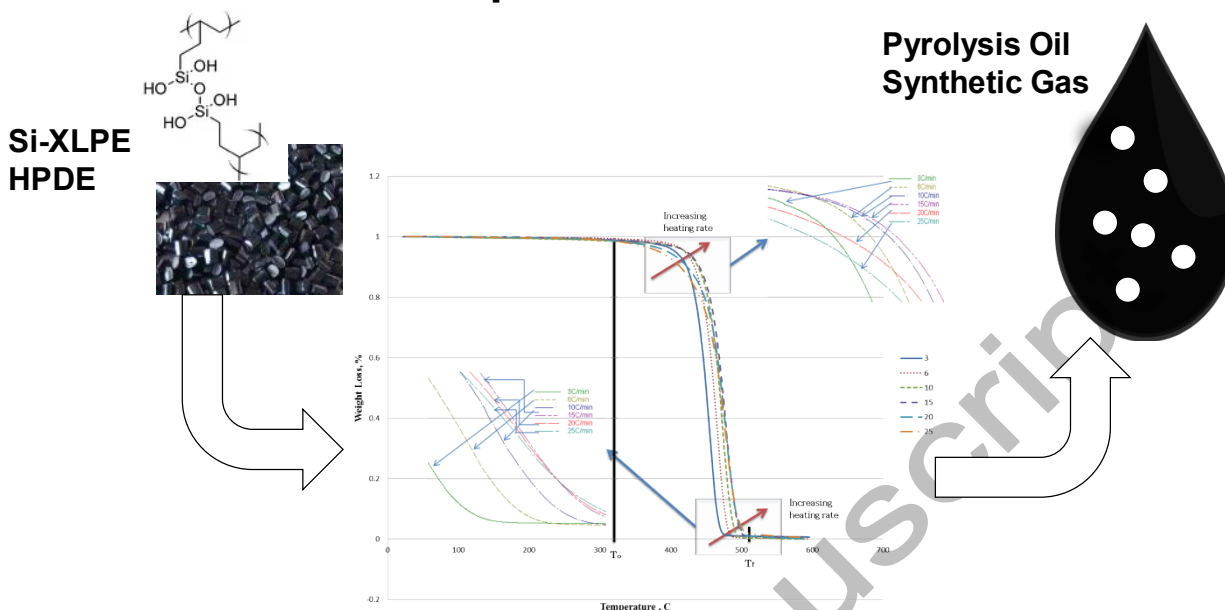
## Kinetic Study on Thermal Degradation of Crosslinked Polyethylene Cable Waste

**Cite this Accepted Manuscript (AM) as:** Accepted Manuscript (AM) version of M. Alshrah, I. Adeyemi, I. Janajreh, Kinetic Study on Thermal Degradation of Crosslinked Polyethylene Cable Waste, Journal of Polymer Research <https://doi.org/10.1007/s10965-022-03101-7>

This AM is a PDF file of the manuscript accepted for publication after peer review, when applicable, but does not reflect post-acceptance improvements, or any corrections. Use of this AM is subject to the publisher's embargo period and AM terms of use. Under no circumstances may this AM be shared or distributed under a Creative Commons or other form of open access license, nor may it be reformatted or enhanced, whether by the Author or third parties. See here for Springer Nature's terms of use for AM versions of subscription articles: <https://www.springernature.com/gp/open-research/policies/accepted-manuscript-terms>

The Version of Record of this article, as published and maintained by the publisher, is available online at: <https://doi.org/10.1007/s10965-022-03101-7>. The Version of Record is the version of the article after copy-editing and typesetting, and connected to open research data, open protocols, and open code where available. Any supplementary information can be found on the journal website, connected to the Version of Record.

## Graphical Abstract



## Kinetic Study on Thermal Degradation of Crosslinked Polyethylene Cable Waste

M. Alshrah<sup>1</sup>, I. Adeyemi<sup>3</sup>, I. Janajreh<sup>2\*</sup>

\*[Isam.Janajreh@ku.ac.ae](mailto:Isam.Janajreh@ku.ac.ae)

<sup>1</sup>Department of Mechanical Engineering, Massachusetts Institute of Technology (MIT),  
Cambridge, USA

<sup>2</sup>Mechanical Engineering Department, Khalifa University,  
Abu Dhabi, UAE

<sup>3</sup>Chemical Engineering Department, Khalifa University,  
Abu Dhabi, UAE

**Abstract:** Kinetic study of the pyrolysis of waste plastic is crucial in the design of an efficient and predictable thermochemical conversion system amidst the huge amount of plastic waste being rejected daily. Here, the chemical kinetics of cross-linked polyethylene under pyrolysis condition is conducted. The thermal degradation of the cross-linked LDPE/Si-XLPE was investigated under two different conditions: dynamic and isothermal heating. Moreover, two popular models of Kissinger and Flynn-Wall-Ozawa were used to infer the activation energy and pre-exponential constant during the dynamic heating at different heating rates. The isothermal conditions were tested at four different temperatures and reaction times based on the Arrhenius kinetic parameters. Thermo-gravimetric results showed the main region of weight loss occurs between 450 and 480 °C which corresponds to the highest conversion rate. The computed activation energies were 290.26 kJ/mole and 287.56 kJ/mole for Kissinger and Flynn-Wall-Ozawa models, respectively.

The dynamic heating produced slightly different values than the one obtained from isothermal heating. This is because the kinetic parameters are highly dependent on the reaction time. These results suggest that Si-XLPE, which is commonly used in the cable industry, follows a similar behavior to the LDPE. This was demonstrated by the detailed analysis of the composition, melting point, thermal stability and thermal degradation.

**Keywords:** Pyrolysis; Thermal degradation; Kinetic study; Recycling; Cross-linked polyethylene.

## 1. Introduction

Plastic industries draw nearly 3% of the total petroleum production [1], and this significant demand for plastic is projected to increase even further. According to the International Energy Agency [2], plastic production is estimated to rise from 322Mt in 2015 to 589Mt in 2050 (Fig. 1). This elevated production is attributed to demands from developing economies and the difficulty in finding substitutes for plastics. Consequently, plastic waste constitutes 10-12% of domestic/municipal solid waste [3]. Polyethylene waste is the major portion of the plastic wastes, accounting for 175.4Mt of the total global production by 2050 [2] and reaching nearly 29% of the total plastic waste in Europe [4]. The packaging and cable industry has the lion share of this waste. The latter reject nearly 5% of their product as run-out and sheathing of discarded cables [5]. Previous attempts to valorize waste plastic were conducted to assess the decline in the mechanical properties of re-processed polypropylene and cross-linked polyethylene materials [5-8] and potential compensation with additives and fillers [9]. Although reuse of plastic can reduce their environmental impact [10], these products are viewed as less competitive in the market place. Moreover, stringent manufacturing practices and adapted international standards place more constraints on plastics treatment. Hence, there is urgent need for efficient plastic recycling through fuel derived plastic waste that can also avoid traditional landfilling disposal. Alternatively, thermal conversions of plastic into fuel-based substitute (referred to as tertiary recycling) could be sought.

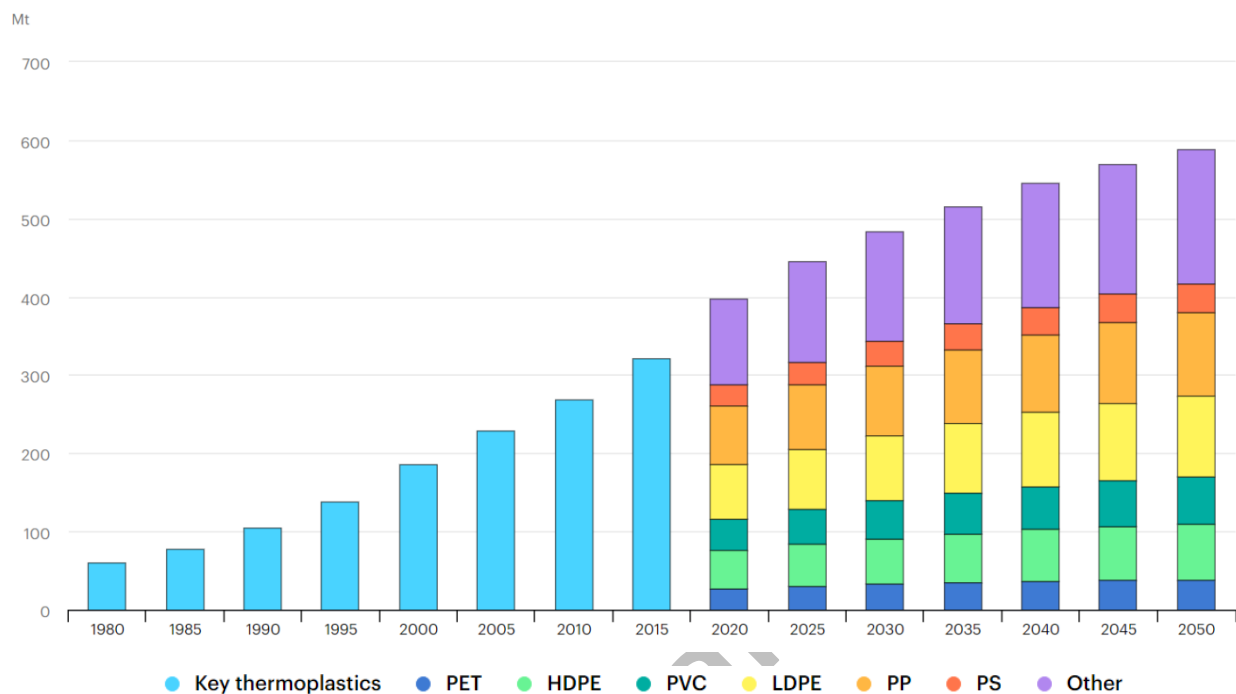


Fig. 1. Production of thermoplastics 1980-2050 [2]

Generally, there are three methods applied to polymers in order to improve their strength and resistance: crystallization, cross-linking, and increasing inherent stiffness of polymer molecules [6]. The cross-linking of polymer initiates the transitioning of thermoplastic into a thermoset plastic. Depending on the degree of cross-linking, a significant change to the properties of the plastic may endure. Silane cross-linked polyethylene (Si-XLPE) is a thermoset resin, used as insulation for electrical cables for its dielectric properties. Si-XLPE is formed by the infusion of siloxane bonds (Si-O-Si) into low density polyethylene (LDPE). It is a highly cross-linked PE which when subjected to heat starts to degrade, or burn rather than melt. Thermal degradation of polyethylene occurs by random chain scission mechanism promoted for the formation of a smaller monomer [11]. Random scission degradation may be described in terms of first order kinetics when the number of chain scission is measured by the change in the degree of polymerization. However, when measured by weight loss, the kinetics deviates from first-order model [2].

Kinetic study of the thermal decomposition of plastic residue in an inert environment has been investigated by several researchers [12-17]. These studies adopted different heating method either following isothermal condition or dynamic heating process. In their study, Das and Tiwari [12]

studied the thermal degradation of four different plastic types under nitrogen inert atmosphere. The plastics includes poly(lactic acid), low density polyethylene (LDPE), high density polyethylene (HDPE) and polypropylene. The degradation occurred under dynamic conditions with nitrogen flow rate of 60 mL/min, heating rate between 5-50 C/minute and particle size of 1-2 mm. They reported that poly(lactic acid) exhibited lower activation energy of 99-116 kJ/mol as compared to polypropylene (133-173kJ/mol), LDPE (170-232kJ/mol), and HDPE (143-231kJ/mol) based on advanced iso-conversional model. In another study, Das and Tiwari [13] conducted the thermogravimetric analysis of polyethylene terephthalate from soft drink bottle waste with nitrogen as the inert gas. Under non isothermal conditions, 20% residue was left after the pyrolysis of the plastic. Moreover, through the advanced iso-conversional model, an activation energy of 203-355 kJ/mol and 196-217 kJ/mol were obtained under non isothermal and isothermal conditions, respectively. In their work, Tondl et al [14] conducted the pyrolysis of a waste marine plastic which was evaluated as containing 91.85% of polypropylene, 3.9% of HDPE, 3.9% of LDPE, 0.1% of polyethylene terephthalate and 0.3% of poly(vinyl chloride) using argon as the inert purge gas. The plastic waste was classified into three categories: small microplastics (less than 1mm), large microplastics (1-4 mm) and mesoplastics (4-25 mm). The argon flow rate was set as 50 mL/min, heating as 5-20 K/min and temperature as 34-1000 C. They reported that the degradation was in a single stage between 700 and 780 K. Moreover, the mesoplastics showed higher activation energy of 338-344 kJ/mol as compared to the small microplastics (320-325kJ/mol) and large microplastics (329-334kJ/mol). Modeling the pyrolysis requires accurate analysis of the kinetic reaction data, including activation energy, pre-constant, and reaction order. In one study, Singh et al [18] studied the kinetics of the pyrolysis of cross linked polyethylene (XLPE). However, they utilized non-isothermal conditions and the Vyazovkin integral iso-conversional method was used to determine changes in the activation energy with the extent of conversion. Du et al [19] investigated the kinetics of the pyrolysis of irradiation cross-linked polyethylene with carbon black filler (CB-PEX) and irradiation cross-linked polyethylene (PEX) through thermo-gravimetric study. They observed that CB-PEX requires more thermal energy than PEX during pyrolysis. The study is based on isothermal study at 10 C/min. Although there exist some kinetic studies of cross linked polyethylene in the literature, these evaluations (isothermal and dynamic) are few and require further assessment for the attainment of comprehensive insights on the pyrolysis of these plastics [18-20].

Hence, in this work, the kinetic study of the thermal degradation (pyrolysis) of waste Si-XLPE was conducted under dynamic and isothermal conditions. The kinetic data are obtained at different temperatures and reaction time through thermo-gravimetric analysis. This study seeks to aid fundamental understanding of the pyrolysis reaction, as well as the generation of fuel oil that can be upgraded to diesel fuel. This is an attempt to reduce the energy demand and improve the sustainability index of the cable industry towards achieving zero waste targets and lowering their process energy demands.

## 2. Materials and methods

The cross-linked polyethylene Si-XLPE waste used in this work was obtained from Ducab Inc. in Abu Dhabi, United Arab Emirates. The degree of crosslinking (DC) is commensurate with the number of groups that interconnect the material, and it is typically given as molar percentage. Specifically, under the presence of the tin catalyst, the reaction of the moisture and alkoxy silyl groups form crosslink between the polymer chains in a single step using a mixture of Vinylsilane-peroxide and antioxidant which mixed with the polyethylene melt prior to conventional cable and pipe extrusion and before the final water-bath curing. The structure of the alkoxy silyl is important in the formation of the crosslink between the polymer chains. Due to the presence of alkoxy group, are able to be hydrolyzed to form silanol based compounds, which are not stable. Thus, they undergo condensation which enables hydrogen bonding, and the subsequent siloxane linkages after drying of the water, to be established. The collected samples were formulated from the PE, Silane (silane peroxide) and Antioxidant formula. They were prepared according to Monosil process at 96-97%, 2-3% and 1 %, respectively. The Si-XLPE samples were prepared for kinetics study using continuous band saw running at a relatively low speed (0.6 m/s) and with relatively coarse teeth, producing thin filaments of Si-XLPE waste of 1-10 mm in length. The filaments were produced through running the band saw at low speed through a large plastic waste chunk (20 cm x 15 cm x 10 cm) at several passes. The plastic yarns are then collected and sieved to 1 mm size.

### 2.1 Experimental setup and material characterization

The DSC/TGA Q600 thermal analyzer was used to perform the Thermogravimetric, derivative thermogravimetric (DTG) and differential scanning calorimetry (DSC) analyses. The experiments were performed under pyrolysis conditions with compressed nitrogen (N<sub>2</sub>) as purging gas of flow rate of 100ml/min while cooling was done using also pure compressed and dried air. Sample sizes of  $\sim 15 \pm 2$  mg were used in all the conducted experiments to avoid any weight/size degradation dependency. Initially, the TGA was calibrated using calcium oxalate monohydrate. Thereafter, the experiments were done in triplicate to assess the reproducibility of the experimental results and to ensure reasonable consistency within standard errors of  $\pm 0.85$  °C. The LDPE samples were placed on the TGA balance arm and equilibrated at 50 °C for 2 minutes, then the temperature was ramped at the five fixed heating rates of 3, 6, 10, 20 and 25 °Cmin<sup>-1</sup> for dynamic condition to the stipulated limit. The temperature was then maintained at isothermal condition for 5 minutes, and thereafter left to cool down to the starting environment temperature. The isothermal test was carried out at different temperatures of 350, 375, 400, 425 °C and reaction time of 15, 20, 30, 45 min, respectively. The relative humidity level in the atmosphere during the experiment has a mean value of 50%. The reaction time was calculated after reaching the desired reaction/test temperature. The conversion percentages of the samples were measured after reaching. The isothermal test was carried out at different temperatures of 350, 375, 400, 425 °C and reaction time of 15, 20, 30, 45 min. The reaction time was calculated after reaching the desired reaction/test temperature. The conversion percentages of the samples were measured after reaching the final reaction temperatures.

The material characterization methods utilized are proximate and ultimate analysis. These tests were conducted to determine the thermal operation range and the sample waste compositions. Thermal analysis represents a broad spectrum of analytical techniques designed to assess the response of materials to temperature change [21]. The analysis was conducted using Simultaneous Thermal Analyzer (STA) in which the device was combined with Thermogravimetric Analysis (TGA) for proximate analysis on the sample and Differential Scanning Calorimetry (DSC) for thermal analysis. Ultimate analysis was conducted to provide the elemental composition of the samples in terms of molar percentage of C, H, S, N, and O. The test was done using Thermo Scientific Flash 2000 Organic (CHNS-O) Elemental Analyzer. Nitrogen was used as purging gas at a flow rate of 100 mL/ min, and air was used as cooling agent for the proximate analysis. The samples (3 mg of Si-XLPE) are subjected to low heating rate of 2 °C/min with enough time to



surpass the sample melting point, i.e. 200 °C for the DSC measurements. In TGA, the samples were subjected to 5 °C /min heating rate until they reach 600 °C to provide the sample fractions (moisture, volatile, fixed carbon and inorganic ash).

## 2.2 Chemical kinetics

The thermal conversion of Si-XLPE was analyzed with the Kissinger based and Flynn-Wall-Ozawa kinetic based models [22]. Both models assume the rate conversion  $\left(\frac{dx}{dt}\right)$  is a linear function with a rate constant  $K$ , and the temperature is an independent function of the conversion ( $x$ ) [21].

$$dx/dt = KF(X) \text{ With } F(x) = (1 - X)^n \quad (1)$$

Where  $n$  represents the reaction order and  $K$  is Arrhenius rate constant which is expressed as:

$$K = Ae^{\left(\frac{-E_a}{RT}\right)} \text{ where } E_a \text{ is the activation energy, } A \text{ is pre-exponential factor and } R \text{ is the gas constant } (R=8.314 \text{ 4621 J/mole K}).$$

Combining all the equation with the assumption that the conversion rate is proportional to sample concentration provides:

$$\frac{dx}{dt} = Ae^{\left(\frac{-E_a}{RT}\right)}(1 - X)^n \quad (2)$$

$$\frac{dx/dt}{(1 - X)^n} = Ae^{\left(\frac{-E_a}{RT}\right)} \quad (3)$$

Taking the natural logarithm for both sides in equation (3), provides a new equation for isothermal condition to calculate the kinetic parameters.

$$\ln\left(\frac{dx/dt}{(1 - X)^n}\right) = \ln(A) - \frac{E_a}{RT} \quad (4)$$

Plotting  $\ln\left(\frac{dx/dt}{(1 - X)^n}\right)$  versus  $1/T$  provides a linear graph with a slope of  $\frac{-E_a}{R}$  and an intercept represented by  $\ln(A)$ . The kinetic parameter is highly dependent on time and reaction order, hence, it was assumed that the reaction follows the first order path. For non-isothermal condition, the heating rate of  $\beta = dT/dt$  was introduced into (2) as follows:

$$\frac{dX}{dT} = \frac{A}{\beta} e^{\left(\frac{-E_a}{RT}\right)} F(X) \quad (5)$$

$$\frac{dX}{F(X)} = \frac{A}{\beta} e^{\left(\frac{-E_a}{RT}\right)} dT \quad (6)$$

In integral form, the differential equation will give a conversion of [23]:

$$g(x) = \int_{X_0}^x \frac{dX}{F(X)} = \frac{A}{\beta} \int_{T_0}^{T_f} e^{\left(\frac{-E_a}{RT}\right)} dT \quad (7)$$

Where  $X_0$  is the initial concentration,  $X_f$  is the final concentration,  $T_0$  is the initial temperature and  $T_f$  is the final temperature.

Kissinger method was used to determine the activation energy for solid state reactions subjected to different heating rates. The activation energy was extrapolated from plots of natural logarithm of heating rate and inverse of the temperature at which the maximum conversion occurred ( $T_p$ ). The activation energy is determined without the need for the calculation of the reaction order as shown below:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) + \ln(1 - X)^{n-1} - \frac{E_a}{RT_p} \quad (8)$$

Where the slope of the plot of  $\ln\left(\frac{\beta}{T_p^2}\right)$  versus  $\frac{1}{T_p}$  line provides the activation energy of the reaction.

Flynn-Wall-Ozawa method is suited for dynamic heating condition. Integrating equation 7 with Doyle approximation [15] will result in equation (9), which was used to calculate activation energy without reference to the reaction order and for different conversion values.

$$\log\beta = \log\left(\frac{AE}{g(X)R}\right) - 2.315 - 0.457 \frac{E_a}{RT} \quad (9)$$

The activation energy was calculated from the slope of the plot of  $\log\beta$  versus  $\frac{1000}{T}$ .

### 3. Results and Discussion

#### 3.1 Proximate and thermal (STA) analysis

The TGA results at temperatures close to 600°C temperature are presented in figure 1, and the data summary showing the proximate composition of the sample is listed in Table 1. The moisture is

entrapped into the small waste filaments from the surrounding humid air, whereas the baseline granular samples resulted in a zero-moisture value for LDPE.

Table 1: STA measured data for Si-XLPE reaching 600°C

Tested samples	Waste Si-XLPE	LDPE
Moisture	1.327%	0.000%
Volatile	98.235%	98.946%
Fixed carbon	0.269%	0.374%
Unburned ash	0.168%	0.679%
T (melt), °C	109.76	109.15
T <sub>o</sub> (decomposition), °C	460.73	462.43
$\Delta h$ (vaporization), J/g	15.10	20.98

The large volatile and low fixed carbon fractions for both LDPE and Si-XLPE are typical characteristics of the plastic. The volatile fraction exceeds 98% while the fixed carbon fraction is less than 0.5% on mass basis. The high volatile content qualifies plastic as an ideal feedstock for pyrolysis, usually at a temperature slightly above the onset of decomposition ( $\approx 450^\circ\text{C}$ ). Pyrolysis acts as a substitute for the high temperature conversion process (i.e. gasification), and produces stable liquefied fuel [24]. The fuel is produced with lower energy penalty by preventing downstream compression and liquefaction of syngas. The extent of the thermal stability of the plastic as shown in figure 1 was over thrice the value of the melting point. It shows that the onset of decomposition extends further beyond the melting point, suggesting the low degree of infused cross-linking. As the temperature surpass 400°C, decomposition takes place very rapidly for the baseline and XLPE. And as the temperature reached 500°C, nearly all the material is released into volatile.

### 3.2 Ultimate analysis (FLASH)

The Flash CHNS/O average results of the analysis of four separate samples of the Si-XLPE waste are presented in Table 2.

Table 2: Elemental composition in mass percentages for Si-XLPE and LDPE samples reaching 1100°C

Si-XLPE	N%	C%	H%	O%	Moist%	Ash/Inorg %	Total %	Molecular formula/HHV
Avg.	0.04	83.6	14.1	0.040	1.327±0.04	1.83	100	HHV 45.775MJ/kg
	7	±0.2	±0.1	8	04	±0.14		
	±0.0			±0.04				
	3							
Ash/Moi st Free (AF)	0.04 8	85.1	14.4	0.415	-----	-----	100.0	C <sub>0.851</sub> H <sub>0.144</sub> O <sub>0.00415</sub> N <sub>0.00048</sub>
<b>LDPE</b>								
Avg.	0.04	84.6	14.4	0.234	0.00	0.723±1.2	100.0	HHV 46.46MJ/Kg
	3	±0.1	±0.0	±0.01				
	±0.0		9					
	1							
Ash Free (AF)	0.04 4	85.2 1	14.5 1	0.24	-----	-----	100.0	C <sub>0.8521</sub> H <sub>0.145</sub> O <sub>0.0024</sub> N <sub>0.00044</sub>

The ultimate composition of the Si-XLPE obtained from experiments showed reasonable agreement with those reported by Encinar and Gonzalez [25]. In general, the results show that Si-XLPE waste contains a high percentage of carbon compared to oxygen and hydrogen contents which signifies its high calorific value and conversion feasibility. Furthermore, it can be observed that Si-XLPE waste lacks sulfur and holds insignificant quantity of inorganic which is attributed

to the silicon. This amount is typically limited so as not to exceed 1% in order to ensure high degree of cross-linking. It is also important to emphasize the accompanying fraction of O due to Si-O-Si bonds. The high heating value HHV can also be calculated using Channiwala and Parikh formula [26] which is given by:

$$\text{HHV} \left( \frac{\text{MJ}}{\text{kg}} \right) = 34.91 \times C + 117.83 \times H - 10.34 \times O - 1.51 \times N + 10.05 \times S - 2.11 \times \text{Ash} \quad (10)$$

Based on the estimation, a high heating value of nearly 45.77 for XLPE and 46.36 MJ/Kg for the LDPE were obtained. This emphasizes the high heating value of the waste plastic, which is equivalent to that of diesel fuel.

### 3.3 Dynamic experiment (STA pyrolysis)

The results of the thermo-gravimetric (TG) analysis for Si-XLPE waste at different heating rates are depicted in Fig. 2. It shows that the heating rate has a considerable influence on the onset of pyrolysis temperature in a way that it shifts the decomposition to higher temperature, and it was triggered by the inhomogeneous and rapid surface heating.

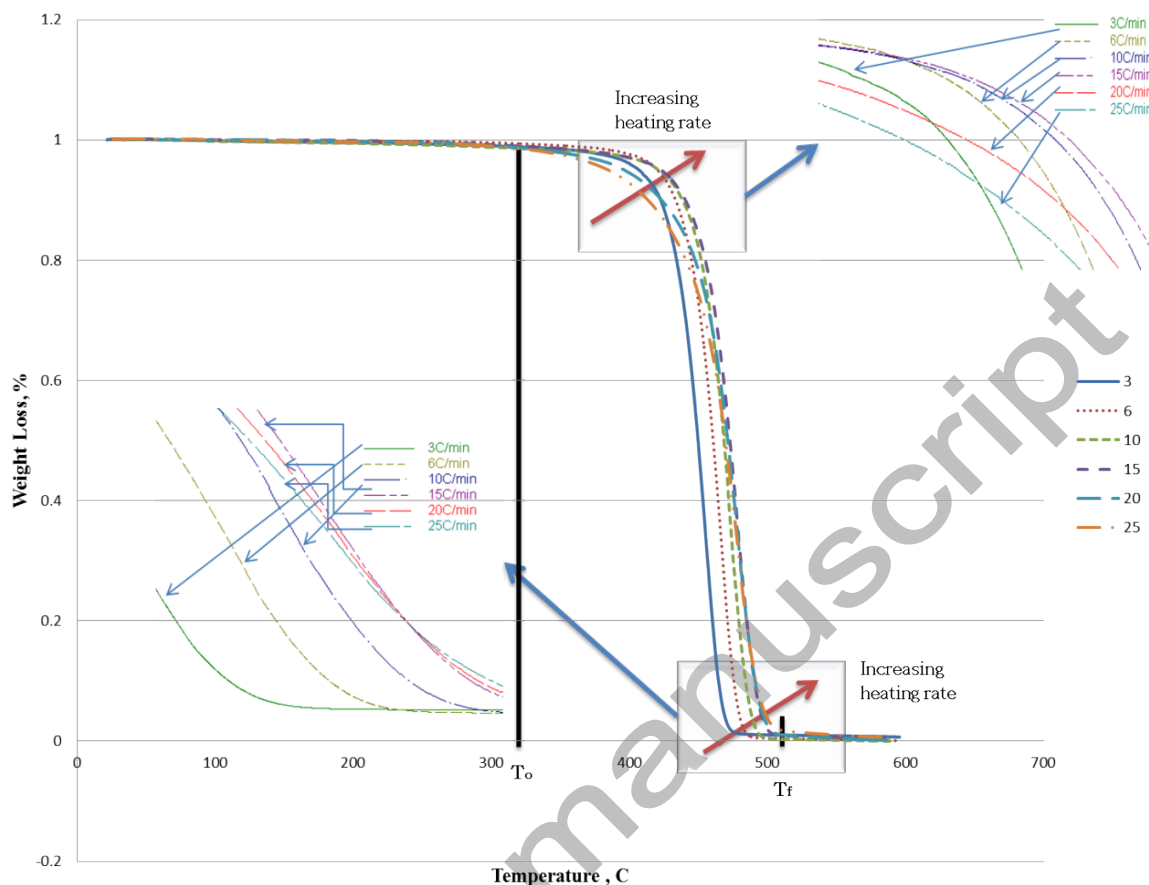


Fig. 2. TG curves for Si-XLPE at different heating rates

The thermal degradation of Si-XLPE is clearly influenced by the heating rate as shown in the TG curve. It shows that the higher heating rate initially shifts the onset of degradation temperature to a higher value before this trend is reversed when a high heating rate is reached (20°C/min). At that heating rate, the degradation temperature starts to reduce. This can be attributed to the initial inhomogeneous and progressive particle heating from the surface towards the core where the low heating rate is insufficient and slow to conduct the TGA heat to the core of the particle. Notably, plastic is characterized with a low conductivity in solid state. At high rate of about 20°C /min, the high temperature gradient between the particle surface and core is “short lived” as it was overcome by the high heating, and consequently a reversion in this trend may potentially occur.

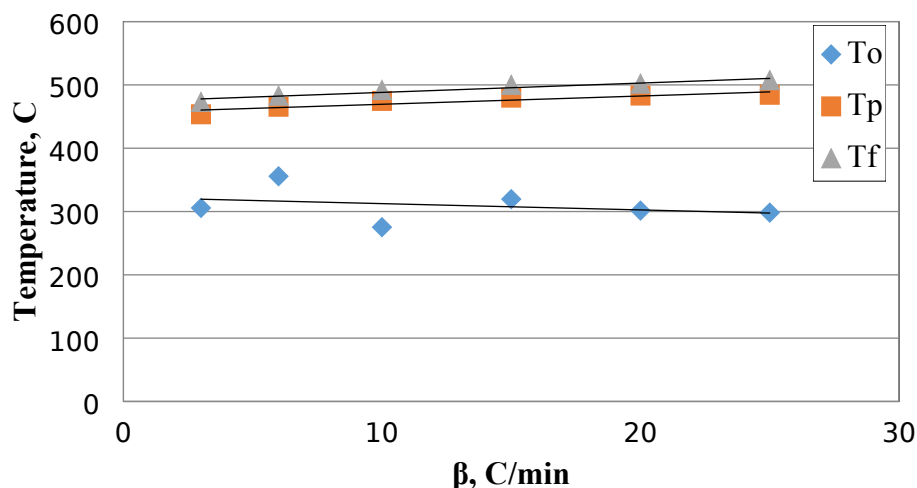


Fig. 3. Thermal decomposition temperatures versus heating rate

Three temperatures were selected to provide more insight to the relation between the heating rates and reaction temperatures as shown in Fig. 3 above. These temperature values were taken at the onset ( $T_o$ ), middle ( $T_p$ ), and the end ( $T_f$ ) of pyrolysis. The values of  $T_o$ ,  $T_p$ , and  $T_f$  can be predicted for Si-XLPE samples at any heating rate by linear fitting of the data as presented in Fig. 3., which yields the following equations:

$$T_o = -0.95958 \beta + 322.45 \quad (11)$$

$$T_p = 1.3042 \beta + 456.38 \quad (12)$$

$$T_f = 1.4723 \beta + 473.46 \quad (13)$$

Where  $T$  is expressed in  $^{\circ}\text{C}$  and  $\beta$  is expressed in  $^{\circ}\text{C}/\text{min}$

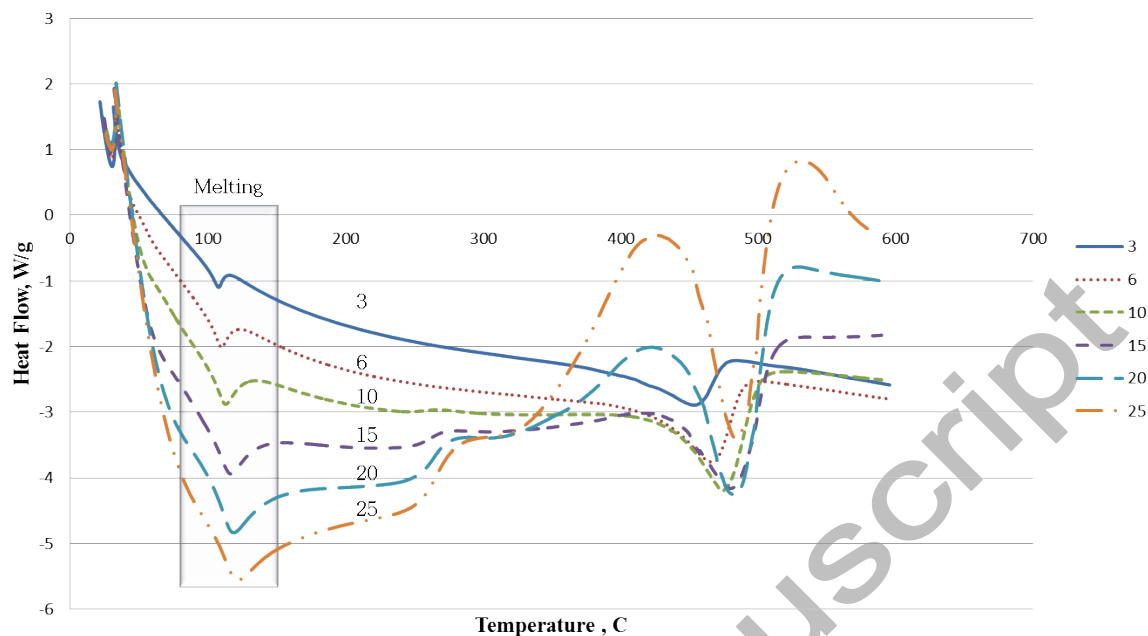


Fig. 4. DSC curves for Si-XLPE at different heating rates

Fig. 4 shows the effect of the heating rate on the decomposition temperature and heat release. The pyrolysis occurs within the temperature range of 450–480 °C as inferred in Table 3. The increase of the heat rate is clearly demonstrated as a shift in the melting point, and likewise in the maximum pyrolysis to higher temperature; The decomposition temperature increases with the increase in the heating rate. This is because when the heating rate is increased, the samples have less residence time at the incremental temperatures. The reduced residence of the samples at the preceding temperatures inhibits the degradation. Hence, the decomposition is delayed to an elevated temperature. This phenomenon has been observed by several studies [29-31]. In their study, Xu et al [29] observed that when the heating rate was raised from 100 to 500 °C/min, the decomposition temperatures increased from 440 to 467 °C and 391 to 454 °C for LDPE and PP, respectively. Similar report could be observed in the study of Singh et al [30] for mixed plastics when the heating rate was increased from 5 to 40 °C/min. Furthermore, Erickson [31] demonstrated that between 5-50 °C/min, the decomposition temperature increased with heating rate for different polymers.



Table 3: DSC decomposition temperature and its heat of diffusion at different heating rate

$\beta$ (heating rate), °C/min	$T_p$ (decomposition), °C	$\Delta h$ (diffusion), J/g
3	453.59	358.37
6	465.49	351.88
10	474.73	262.49
15	479.92	174.12
20	483.17	165.06
25	484.4	156.90

Fig. 5 shows the data representation of each of Kissinger and Flynn-Wall-Ozawa models that allow one to infer the chemical kinetics according to equations (8) and (9). The resulting linear trendline equation for Kissinger model was  $y = 35.895 - 34.911 x$  with correlation coefficient  $R^2 = 0.9811$ , while that for Flynn-Wall-Ozawa was  $y = 22.199 - 15.806 x$  with  $R^2 = 0.9825$ . The activation energy calculated using Kissinger model is found to be 290.2662 kJ/mole. Using Flynn-Wall-Ozawa model, the calculated activation energy was found to be 287.5676 kJ/mole. The values obtained from both models are in general agreement with those reported by Bockhorn et al. (262.1 kJ/mole) [27]. These values are 10.74 % and 9.71 % for Kissinger and Flynn-Wall-Ozawa, respectively.

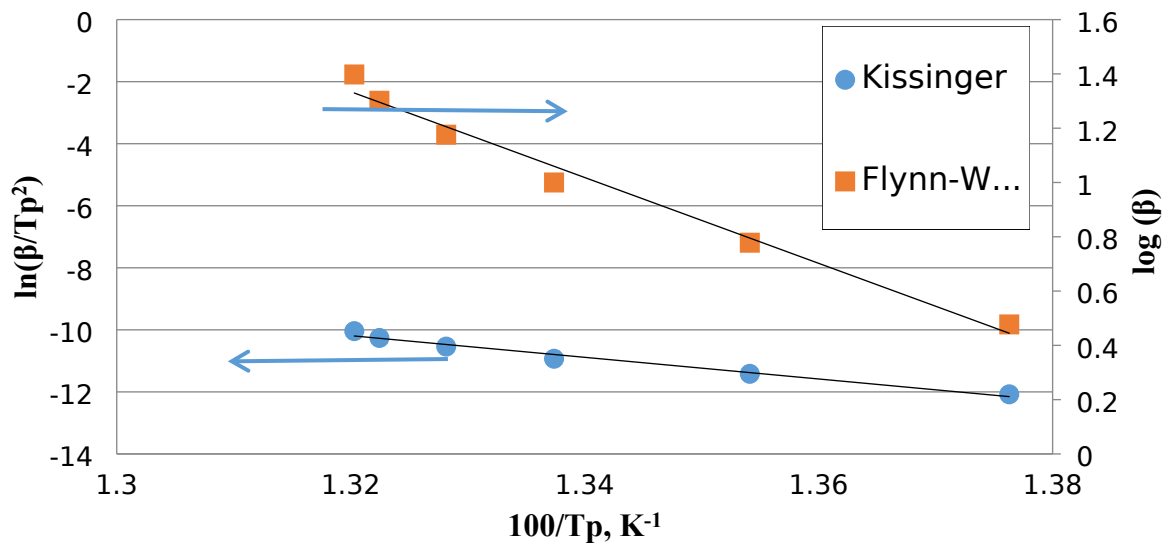


Fig. 5. Representation for each kinetic model versus the temperature

### 3.3 Isothermal analysis

The results of the isothermal analysis for Si-XLPE waste at different temperatures and reaction times are shown in Fig. 6. Results showed the effect of temperature and reaction time on the conversion. With increasing temperature, the conversion was increased at a constant reaction time. In addition, the conversion of XLPE highly depends on reaction time. For instance, when the reaction time was increased, the conversion increased at constant temperature.

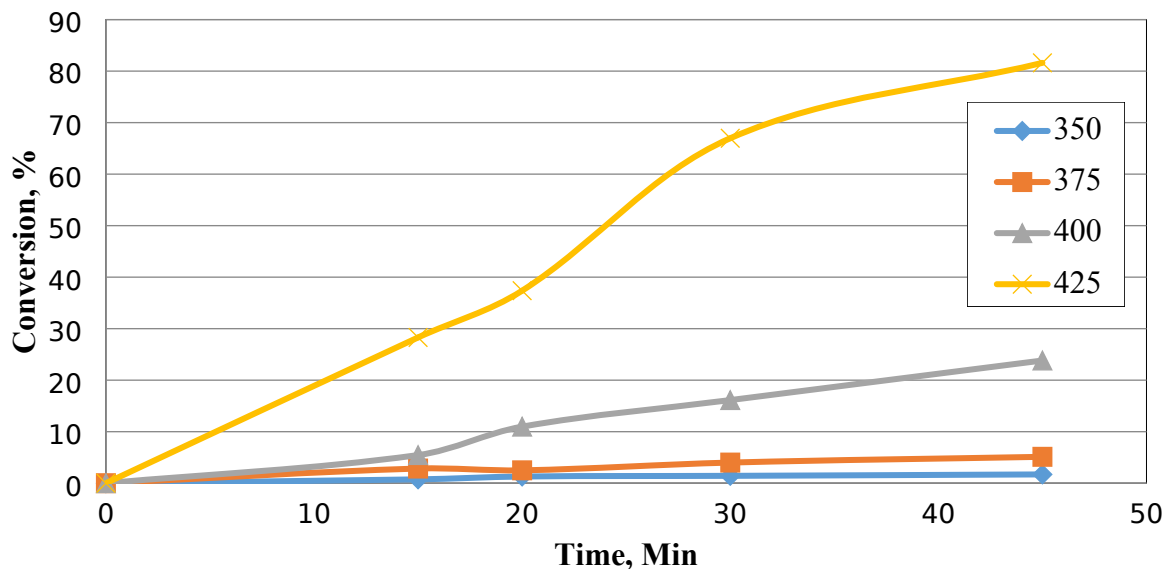


Fig. 6. TG results for isothermal conditions

Kinetic parameters are calculated from the above graph by computing the conversion rate at different reaction order and time. Applying equation (4) provides the activation energy and pre-exponential factor for the pyrolysis reaction. Fig. 7 represents the effect of reaction time and reaction order on the activation energy. Linear relationship was obtained between the activation energy and reaction time. Moreover, the activation energy increased as the reaction order was raised. All the results are summarized in Table 4.

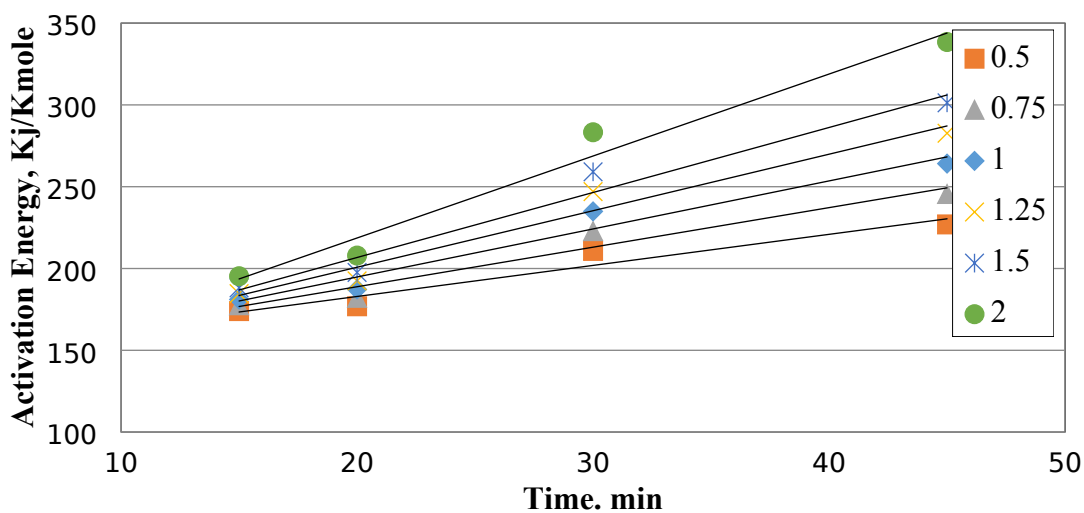


Fig. 7. Activation energy at different reaction time and reaction order

The activation energy with first order reaction assumption possesses similar values to the one obtained from dynamic analysis. Therefore, the assumption that pyrolysis reaction behavior is first order is a valid one. All the values for the activation energy and pre-exponential factor were both within the range reported by Costa et al., [28]. These results suggest that Si-XLPE follows a similar behavior to the LDPE in terms of composition, melting, thermal stability and thermal degradation.

Table 4: Kinetic parameters at different time and reaction order

Reaction order	Time	Time			
		15	20	30	45
0.5	$E_a$	173.971	176.915	210.738	226.951
	A	1.812E+11	3.382E+11	1.731E+14	3.124E+15
0.75	$E_a$	177.522	182.078	222.827	245.534
	A	3.559E+11	9.021E+11	1.707E+15	1.052E+17
1.0	$E_a$	181.080	187.250	234.916	264.117
	A	6.983E+11	2.408E+12	1.686E+16	3.541E+18
1.25	$E_a$	184.630	192.413	247.006	282.691
	A	1.371E+12	6.423E+12	1.663E+17	1.192E+20
1.5	$E_a$	188.181	197.584	259.095	301.274
	A	2.693E+12	1.714E+13	1.641E+18	4.013E+21
2.0	$E_a$	195.290	207.911	283.282	338.440
	A	1.038E+13	1.219E+14	1.598E+20	4.553E+24

#### 4 Conclusion

The thermal degradation of plastic waste and the characterization of Si-XLPE generated from cable industry was investigated. The material characterization was conducted through different analysis which includes proximate, ultimate, and energy content analysis. The proximate analysis showed Si-XLPE contains mainly volatiles and low fraction of fixed carbon, which qualifies plastic as an ideal feedstock for pyrolysis at relatively moderate temperature (>300°C). The ultimate analysis results showed that Si-XLPE contain a high percentage of carbon compared to hydrogen and oxygen contents and no sulfur content. These elemental contents are contributing factors to its high

calorific value (45MJ/kg). A thermo-gravimetric method was implemented to calculate kinetic parameters under two different conditions: dynamic and isothermal heating. The dynamic method showed distinctly different thermal decompositions depending on the process heating rate. The results showed an increase in the initial degradation temperature and a shift in the maximum decomposition temperature towards higher temperature when the heating rate is increased. The dynamic condition showed that the pyrolysis for plastic occurs within the temperature range of 450 – 480 °C. Isothermal condition showed the relationship between conversion, and reaction temperature and time. When increasing the reaction time or temperature, the conversion and kinetic parameters increased. Kinetic parameters differ for the two conditions but remains in close proximity and within acceptable range. For dynamic condition, two different models were used: Kissinger and Flynn-Wall-Ozawa. However, Arrhenius equation is used to quantify the activation energies and the pre-exponential factor at different reaction time for isothermal conditions. Experiments conducted at isothermal condition validate the assumption that the reaction is first order. These results suggest that Si-XLPE follows a similar behavior to the LDPE as shown by its composition, melting point, thermal stability and thermal degradation. This work not only inferred the chemical kinetics of the Si-XPLE waste, but also confirmed the reported literature on the degradation of LDPE.

### **Acknowledgments**

The financial support of Khalifa University is highly acknowledged under grant number xxx2018.

### **Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### **Credit author statement**

M. Alshrah: Experimental and data analysis & interpretation, methodology, software and writing & investigation as well as validation, writing, reviewing and editing

I. Adeyemi: Methodology, data curation, writing, reviewing and editing

Corresponding Author I. Janajreh: Conceptualization and original draft preparation and experimental data analysis & interpretation, methodology, software and writing, investigation & supervision

## Highlights

- Characterization and thermal degradation of the cable industry plastic waste is investigated
- TGA method is used to infer kinetic parameters under dynamic and isothermal conditions
- Plastic pyrolysis occurs within the temperature range of 450 – 480 °C
- Si-XLPE follows a similar composition and thermal behavior to the LDPE
- Isothermal conditions validate the assumption that the reaction behave as 1<sup>st</sup> order reaction

## References

1. Stein, R.S., *Polymers, Recycling*, in *Encyclopedia of Physical Science and Technology - Polymers*. p. 745.
2. International Energy Agency. The Future of Petrochemicals: Towards a more sustainable chemical industry. Technology Report, October 2018. <https://www.iea.org/reports/the-future-of-petrochemicals>. Retrieved on the 6<sup>th</sup> of October, 2021
3. Laboratory, W.-t.-E., *Poster Abu Dhabi Waste Current fate and Energy Recovery Options*.
4. Industry, T.E.p., *Plastic - the Facts 2011*, 2010.
5. I.Janajreh, M. Alshrah, S. Zamzam, Mechanical recycling of PVC plastic waste streams from cable industry: A case study, *J. of Sustainable Cities and Society*, Vol. 18, , P. 13-20 (2015), <https://doi.org/10.1016/j.scs.2015.05.003>
6. Vollmer, I., Jenks, M. J., Roelands, M. C., White, R. J., van Harmelen, T., de Wild, P., van Der Laan, G.P., Meirer, F., Keurentjes, J.T. & Weckhuysen, B. M. (2020). Beyond mechanical recycling: Giving new life to plastic waste. *Angewandte Chemie International Edition*, 59(36), 15402-15423.
7. Soto, J. M., Blázquez, G., Calero, M., Quesada, L., Godoy, V., & Martín-Lara, M. Á. (2018). A real case study of mechanical recycling as an alternative for managing of polyethylene plastic film presented in mixed municipal solid waste. *Journal of Cleaner Production*, 203, 777-787.
8. Schyns, Z. O., & Shaver, M. P. (2021). Mechanical recycling of packaging plastics: A review. *Macromolecular rapid communications*, 42(3), 2000415.
9. Sarde, B., Patil, Y. D., & Dholakiya, B. Z. (2021). Evaluation of effectiveness of palm oil fuel ash as green filler and methyl methacrylate as additive in recycled PET resin polymer composite. *Journal of Building Engineering*, 43, 103107.
10. Shahnawaz, M., Sangale, M. K., & Ade, A. B. (2019). Plastic waste disposal and reuse of plastic waste. In *Bioremediation Technology for Plastic Waste* (pp. 21-30). Springer, Singapore.
11. Ray, S., & Cooney, R. P. (2018). Thermal degradation of polymer and polymer composites. In *Handbook of environmental degradation of materials* (pp. 185-206). William Andrew Publishing.
12. Das, P., & Tiwari, P. (2017). Thermal degradation kinetics of plastics and model selection. *Thermochimica Acta*, 654, 191-202.
13. Das, P., & Tiwari, P. (2019). Thermal degradation study of waste polyethylene terephthalate (PET) under inert and oxidative environments. *Thermochimica Acta*, 679, 178340.
14. Tondl, G., Bonell, L., & Pfeifer, C. (2018). Thermogravimetric analysis and kinetic study of marine plastic litter. *Marine pollution bulletin*, 133, 472-477.
15. Nisar, J., Ali, G., Shah, A., Iqbal, M., Khan, R. A., Anwar, F., Ullah, R. & Akhter, M. S. (2019). Fuel production from waste polystyrene via pyrolysis: Kinetics and products distribution. *Waste management*, 88, 236-247.

16. Silvarrey, L. D., & Phan, A. N. (2016). Kinetic study of municipal plastic waste. *International journal of hydrogen energy*, 41(37), 16352-16364.
17. Nisar, J., Ali, G., Shah, A., Shah, M. R., Iqbal, M., Ashiq, M. N., & Bhatti, H. N. (2019). Pyrolysis of expanded waste polystyrene: Influence of nickel-doped copper oxide on kinetics, thermodynamics, and product distribution. *Energy & Fuels*, 33(12), 12666-12678.
18. Singh P, Déparrois N, Burra KG, Bhattacharya S, Gupta AK. Energy recovery from cross-linked polyethylene wastes using pyrolysis and CO<sub>2</sub> assisted gasification. *Applied Energy*. 2019 Nov 15;254:113722.
19. Du Y, Jiang X, Lv G, Jin Y, Wang F, Chi Y, Yan J, Buekens A. TG-DSC and FTIR study on pyrolysis of irradiation cross-linked polyethylene. *Journal of Material Cycles and Waste Management*. 2017 Oct;19(4):1400-4.
20. Mo SJ, Zhang J, Liang D, Chen HY. Study on pyrolysis characteristics of cross-linked polyethylene material cable. *Procedia engineering*. 2013 Jan 1;52:588-92.
21. Lobo, H. and J.V. Bonilla, *Handbook of plastics analysis*. Vol. 68. 2003: Crc Press.
22. Liu, M., et al., *Thermal degradation process and kinetics of poly (dodecamethyleneisophthalamide)*. *Chemical Journal on Internet*, 2003. 5(6): p. 43-45.
23. Núñez, L., et al., *Thermogravimetric study of the decomposition process of the system BADGE (< i>n</i>= 0)/1, 2 DCH*. *Polymer*, 2000. 41(12): p. 4635-4641.
24. I. Janajreh, R.Q., M. Al Shrah. *Pyrolysis of Si-XLPE Waste*. in *The 10th Global Conference on Sustainable Manufacturing*. 2012. Istanbul, turkey.
25. Encinar, J. and J. Gonzalez, *Pyrolysis of synthetic polymers and plastic wastes. Kinetic study*. *Fuel Processing Technology*, 2008. 89(7): p. 678-686.
26. Channiwala, S. and P. Parikh, *A unified correlation for estimating HHV of solid, liquid and gaseous fuels*. *Fuel*, 2002. 81(8): p. 1051-1063.
27. Bockhorn, H., et al., *Kinetic study on the thermal degradation of polypropylene and polyethylene*. *Journal of Analytical and Applied Pyrolysis*, 1999. 48(2): p. 93-109.
28. Costa, P.A., et al., *Kinetic evaluation of the pyrolysis of polyethylene waste*. *Energy & Fuels*, 2007. 21(5): p. 2489-2498.
29. Xu, F., Wang, B., Yang, D., Hao, J., Qiao, Y., & Tian, Y. (2018). Thermal degradation of typical plastics under high heating rate conditions by TG-FTIR: Pyrolysis behaviors and kinetic analysis. *Energy Conversion and Management*, 171, 1106-1115.
30. Singh, R. K., Ruj, B., Sadhukhan, A. K., & Gupta, P. (2019). Impact of fast and slow pyrolysis on the degradation of mixed plastic waste: Product yield analysis and their characterization. *Journal of the Energy Institute*, 92(6), 1647-1657.
31. Erickson, K. L. (2008). Application of Low-Heating Rate TGA Results to Hazard Analyses Involving High-Heating Rates (No. SAND2008-1177C). Sandia National Lab.(SNL-NM), Albuquerque, NM (United States).

Table 5: STA measured data for Si-XLPE reaching 600°C

Tested samples	Waste Si-XLPE	LDPE
Moisture	1.327%	0.000%
Volatile	98.235%	98.946%
Fixed carbon	0.269%	0.374%
Unburned ash	0.168%	0.679%
T (melt), °C	109.76	109.15
T <sub>o</sub> (decomposition), °C	460.73	462.43
$\Delta h$ (vaporization), J/g	15.10	20.98

Table 6: Elemental composition in mass percentages for Si-XLPE and LDPE reaching 1100°C

Si- XLPE	N%	C%	H%	O%	Moist%	Ash/Inorg %	Total %	Molecular formula/HHV
-------------	----	----	----	----	--------	----------------	------------	--------------------------



Avg.	0.04	83.6	14.1	0.040	1.327±0.	1.83	100	HHV 45.775MJ/kg
	7	±0.2	±0.1	8	04	±0.14		
	±0.0			±0.04				
	3							
Ash/Moi	0.04	85.1	14.4	0.415	-----	-----	100.0	C <sub>0.851</sub> H <sub>0.144</sub> O <sub>0.00415</sub> N <sub>0.</sub>
st Free	8							00048
(AF)								
<b>LDPE</b>								
Avg.	0.04	84.6	14.4	0.234	0.00	0.723±1.2	100.0	HHV 46.46MJ/Kg
	3	±0.1	±0.0	±0.01				
	±0.0		9					
	1							
Ash	0.04	85.2	14.5	0.24	-----	-----	100.0	C <sub>0.8521</sub> H <sub>0.145</sub> O <sub>0.0024</sub> N <sub>0.</sub>
Free	4	1	1					00044
(AF)								

Table 7: DSC decomposition temperature and its heat of diffusion at different heating rate

$\beta$ (heating rate), °C/min	T <sub>p</sub> (decomposition), °C	$\Delta h$ (diffusion), J/g
3	453.59	358.37
6	465.49	351.88
10	474.73	262.49
15	479.92	174.12
20	483.17	165.06
25	484.4	156.90

Table 8: Kinetic parameters at different time and reaction order

Reaction order	Time
----------------	------

		15	20	30	45
0.5	$E_a$	173.971	176.915	210.738	226.951
	A	1.812E+11	3.382E+11	1.731E+14	3.124E+15
0.75	$E_a$	177.522	182.078	222.827	245.534
	A	3.559E+11	9.021E+11	1.707E+15	1.052E+17
1.0	$E_a$	181.080	187.250	234.916	264.117
	A	6.983E+11	2.408E+12	1.686E+16	3.541E+18
1.25	$E_a$	184.630	192.413	247.006	282.691
	A	1.371E+12	6.423E+12	1.663E+17	1.192E+20
1.5	$E_a$	188.181	197.584	259.095	301.274
	A	2.693E+12	1.714E+13	1.641E+18	4.013E+21
2.0	$E_a$	195.290	207.911	283.282	338.440
	A	1.038E+13	1.219E+14	1.598E+20	4.553E+24

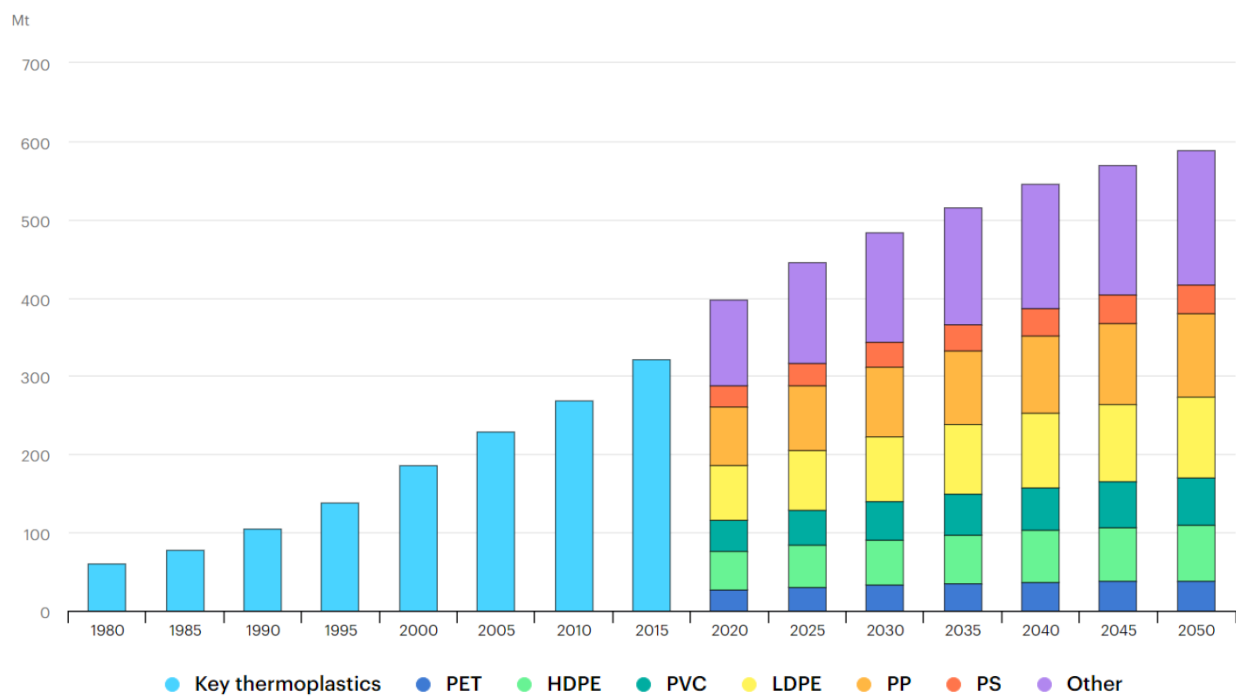


Fig. 1. Production of thermoplastics 1980-2050 [2]

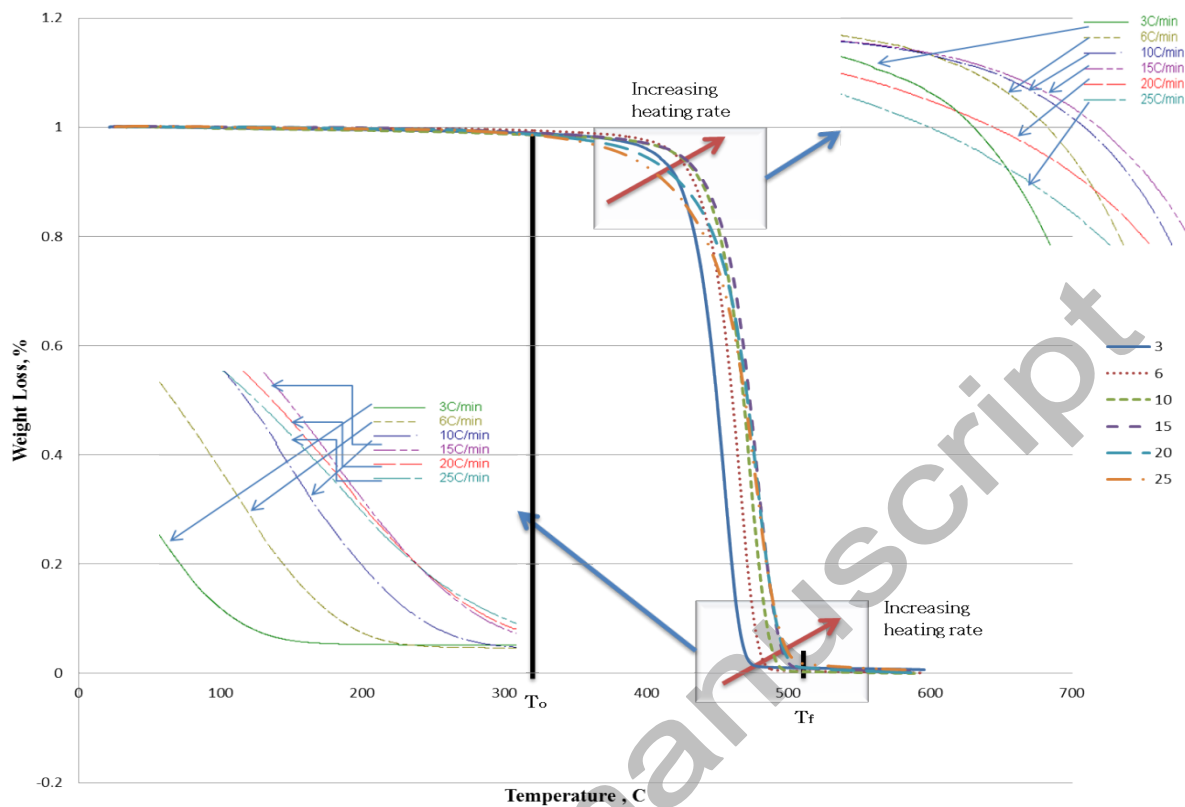


Fig. 2. TG curves for Si-XLPE at different heating rates

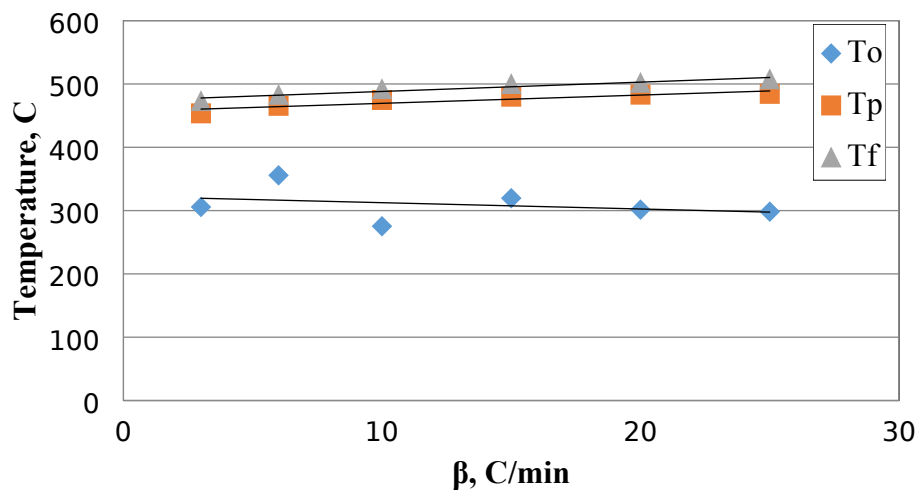


Fig. 3. Thermal decomposition temperatures versus heating rate

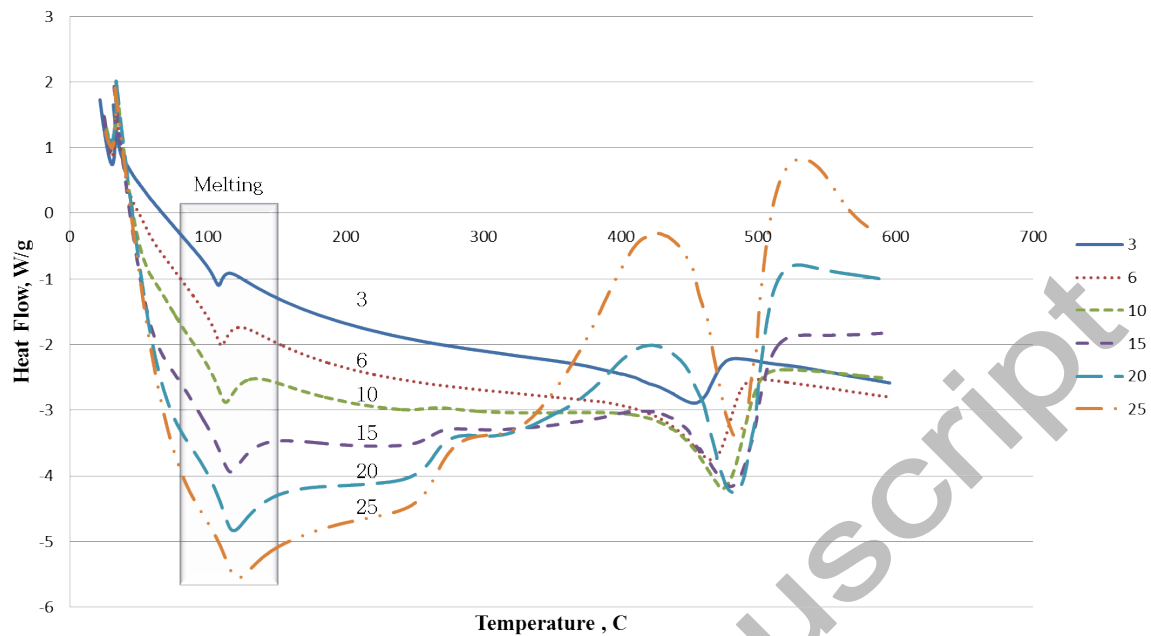


Fig. 4. DSC curves for Si-XLPE at different heating rates

Accepted manuscript

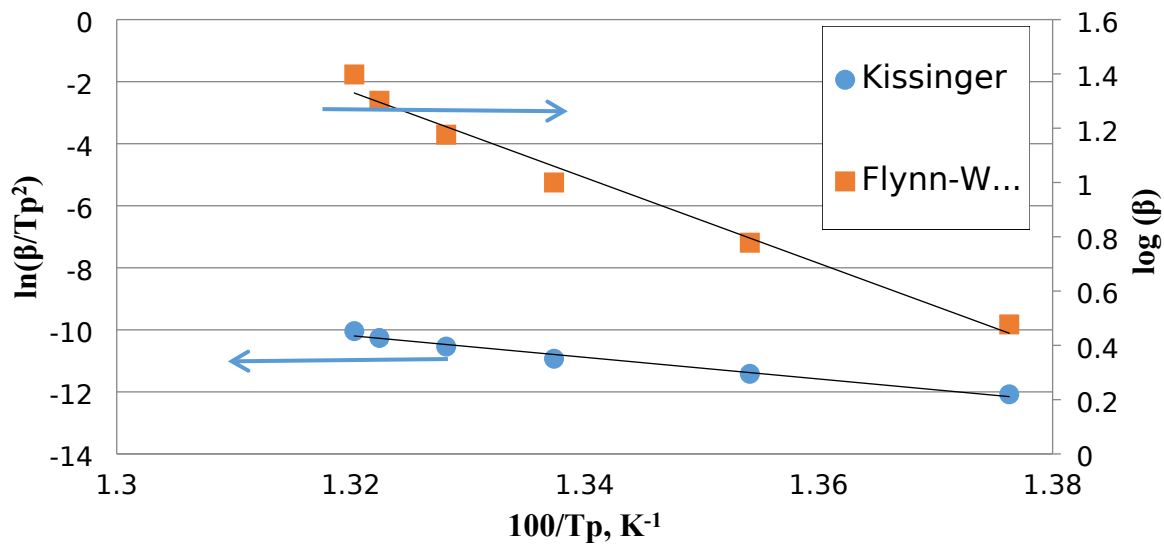


Fig. 5. Representation for each kinetic model versus the temperature

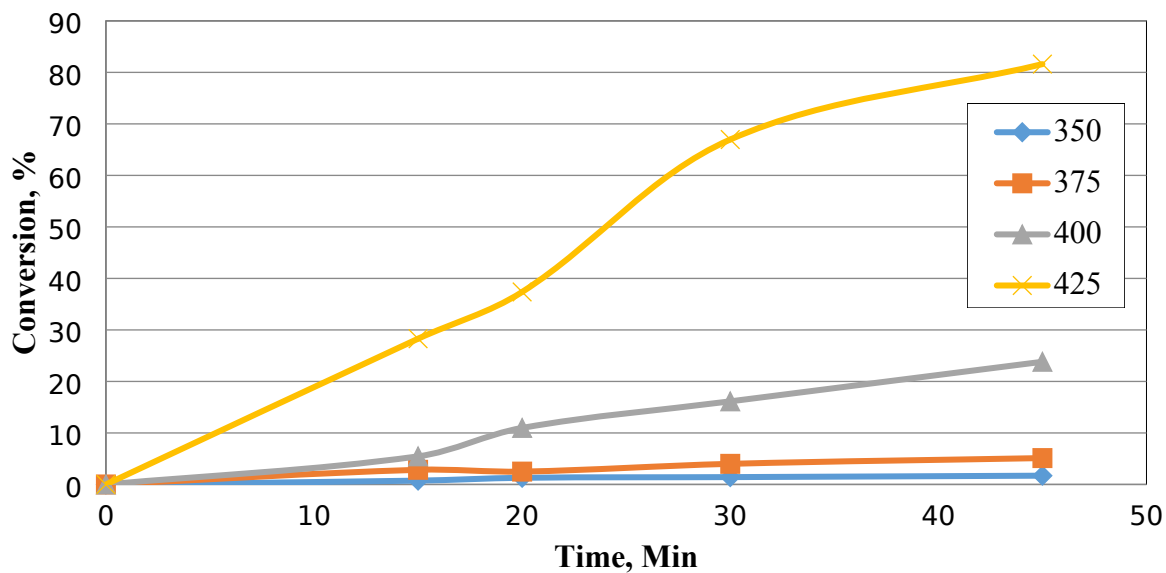


Fig. 6. TG results for isothermal conditions

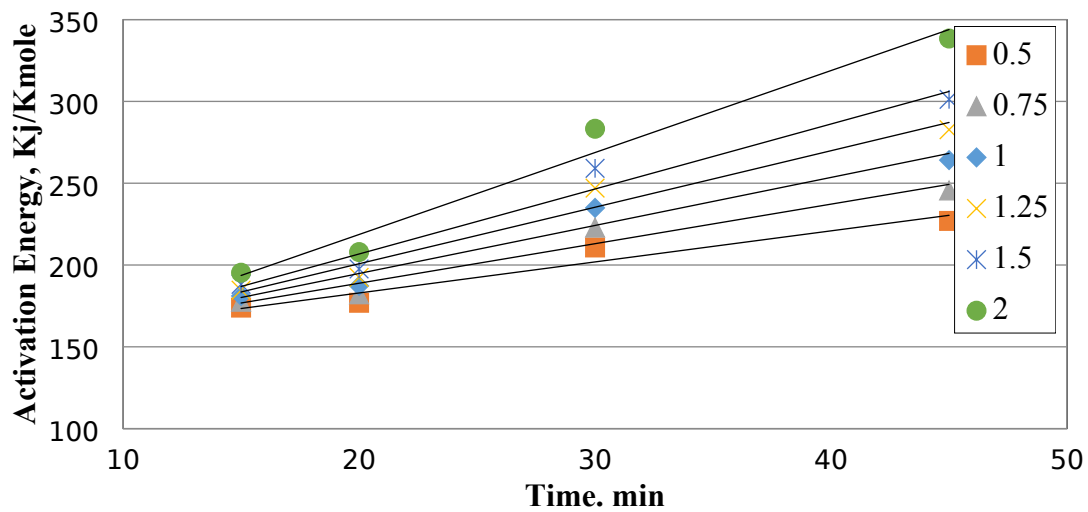


Fig. 7. Activation energy at different reaction time and reaction order

Accepted manuscript