Kinetic Analysis of Thermal Degradation of Polyolefin Mixtures

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Abstract—**Plastic wastes are a global concern for their environmental impacts. A proficiency method for plastic waste management is a chemical recycling through a pyrolysis process. In this work, kinetic analysis of thermal degradation of polyolefin mixture between polypropylene (PP) and low density polyethylene (LDPE) under pyrolysis atmosphere at different compositions was investigated using thermogravimetric analysis (TGA), operated non-isothermally. Besides, Vyazovkin model-free method, together with different temperature integral approximation approaches, was used for kinetic parameter analysis from TGA results. It was found that thermal degradation process of polyolefin mixture was a triple step process and an addition of PP reduced degradation temperature. Besides, different approximation approaches did not affect activation energy value. For polyolefin mixture, the activation energy was increased initially, constant intermediately and finally increased again with increasing conversion. Finally, the activation energy of the polyolefin mixture was lower than those of pure polymers and decreased with increasing PP fraction.**

Index Terms—**Thermal degradation, polyolefin, kinetic analysis, thermogravimetric analysis, Vyazovkin model-free method.**

I. INTRODUCTIONS

Problem of plastic wastes is mainly on an environmental issue due to their extremely slow degradability. Since over 60% of the plastic wastes are polyolefin [1], therefore, it should be useful, if a particular attention can be made on handling the polyolefin plastic wastes. Currently, plastic waste managements are 65 % landfill disposal, 25 % reuse and 10 % recycling both mechanically and chemically [2]. Among these, the chemical recycling method is the most beneficial method for which a production of many valuable products, such as gas and liquid fuel, petrochemical feedstock and monomer, can be obtained through a plastic pyrolysis. In order to design and optimize pyrolytic equipment and the pyrolysis process appropriately, kinetic information of the plastic pyrolysis is necessary and, hence, scientific investigations in this particular area are of importance.

Thermogravimetric analysis (TGA) is one of widely used techniques for the investigation of the kinetics of the thermal degradation of the plastics where, for the kinetic of the plastic pyrolysis, the operation will be carried out under nitrogen atmosphere. And, the operation can be operated in both isothermal [3]-[5] and non-isothermal [5]-[11]. For the

isothermal operation, sample temperature is initially increased rapidly from room temperature to a specific temperature and maintained at that temperature for an entire degradation process. Then, percent weight losses with respect to time, known as TG curve, are recorded. On the other hand, for the non-isothermal operation, the sample is continuously heated at a certain heating rate. The percent weight losses with respect to temperature, also known as TG curves, are recorded. The kinetic information derived from the isothermal operation is useful for flash pyrolysis, while the information from the non-isothermal operation is applicable for a batchwise operation. However, it is noteworthy to address here that the non-isothermal condition is more convenient to operate and is the process applied in this work.

Calculation methods for kinetic parameters from the TG curve can be divided into 2 classes, a model-fitting method and a model-free method, which can be used for the isothermal and the non-isothermal conditions [3]. A feature of the model-fitting method is that, based on rate equation and Arrhenius equation, this method requires an assumption of a reaction model before activation energy and a frequency factor can be interpreted. In addition, the activation energy is varied with only temperature and is an average value for an entire conversion level, even though it can also be changed with the level of the conversion. Besides, the analysis for the kinetic parameters from the non-isothermal condition uses a single heating rate, which may be not sufficient to obtain the correct activation energy. As a result, the kinetic triplets derived from this method are highly uncertain and cannot be compared with the kinetics triplet from the isothermal condition. On the other hands, the model free method has no need for the presumed reaction model. To obtain the accurate activation energy, the TG data of different heating rates are used. In addition, this method allows a variation of the activation energy with respect to both the temperature and the conversion to be revealed. Moreover, this later method is compatible with a complex reaction kinetic [6]. Therefore, the model-free method can be recommended as a trustworthy way to obtain the reliable and consistent kinetic information from the non-isothermal condition. And, it can help to reveal a complexity of multiple reactions due to the dependencies of the activation energy on the extent of the conversion [3], [6], [12].

Considering the non-isothermal model-free method, there are different types of the temperature integral numerical approximation approaches for example Ozawa, Flynn and Wall (OFW) method using a linear approximation (less accurate) utilizing Doyle's approximation [9] and Vyazovkin (VYZ) method using a non-linear approximation (more accurate) [3] utilizing a direct numerical integration method

[11], Cai *et al.* approximation [5], Coats & Redfern approximation, Gorbachev approximation or Agrawal and Sivasubramanian approximation [6]. Between OFW method and VYZ method, VYZ model-free method has become popular because it can bring out the more reliable and consistent kinetic information from the non-isothermal TG data of the polymer degradation [11]. And, this method was applied in this work.

There were many previous works investigated the kinetics of the thermal degradation of the plastics using TGA under the pyrolysis atmosphere (Nitrogen atmosphere) and the non-isothermal condition together with an application of the VYZ model-free method for the kinetic parameter interpretation. Saha *et al.* [5] studied the isothermal and the non-isothermal degradation kinetics of PET waste using various temperature integral approximation approaches such as Coats and Redfern, Gorbachev, and Agrawal and Sivasubramanian and the direct numerical integration to analyze the decomposition kinetics. The results showed that the activation energy was a weak but increasing function with the conversion in case of the non-isothermal condition but was a decreasing function with the conversion in case of the isothermal condition. In addition, the activation energy obtained for the non-isothermal data showed similar results for all types of the approximation approaches (Coats and Redfern, Gorbachev, and Agrawal and Sivasubramanian). Saha and Ghoshal [6] studied the thermal degradation kinetics of polyethylene (PE) waste. In this work, Cai *et al.* temperature integral approximation approach was firstly used along with other approximation approaches which were Coats and Redfern, Gorbachev, Agrawal and Sivasubramanian and the direct numerical integration. They reported that the activation energy increased continuously with increasing conversion. Furthermore, they also addressed that the limiting step of the thermal degradation shifted toward the degradation initiated by random scission leading to the higher activation energy at the higher conversion. In addition, they found that Cai *et al.* approximation approach was the best method among other approximation approaches. Chowlu *et al.* [11] studied the non-isothermal degradation of PP and LDPE mixtures of different ratios (20:80, 35:65, 50:50, 65:35, 80:20) using the direct numerical integration for the temperature integral approximation. They reported that, the activation energy weakly increased with the conversion during the initial degradation stage but, then, became strongly increased with increased the conversion at the later stage until the end of the degradation process. They, finally, proposed that the ratio of PP: LDPE equal to 65:35 was the most preferable composition because of its low activation energy and high amount of light hydrocarbons (≤C10), delivered.

In this work, we investigated the kinetics of the thermal degradation of pure polypropylene (PP), pure low density polyethylene (LDPE) and the mixtures of polyolefin (PP/LDPE), under the pyrolysis atmosphere, using thermogravimetric analysis (TGA). In addition, under the non-isothermal operation, the Vyazovkin model-free method was used to interpret the kinetic parameters from the TG curves. Finally, the kinetic parameters obtained using various temperature integral approximation approaches, which were

Coats and Redfern, Gorbachev, Agrawal and Sivasubramanian and Cai *et al.* approximation, were also compared.

II. EXPERIMENTS

A. Equipment and Materials

Thermogravimetric analyser (TGA) used in this work was Rigaku TGA (TG-DTA8120). Scanning electron microscope was used to observe images of polymer powders. In addition, sieve analysis was used for particle size analysis. Polymers used in this work were polypropylene copolymer (PP, Grade PP1510PC) and low density polypropylene homopolymer (LDPE, Grade LD2026K). All plastics were shredded into a powder form as illustrated in Fig. 1(a) for SEM image of PP and Fig. 1(b) for SEM image of LDPE within a size range of 180 - 250 μm. From the sieve analysis, particle size distributions of PP and LDPE were presented in Fig. 2.
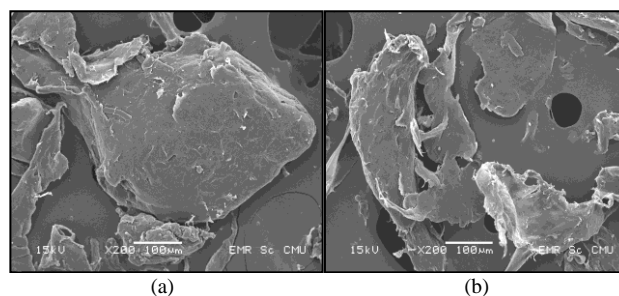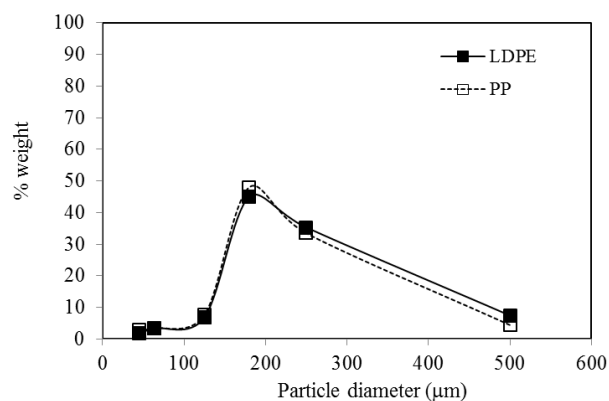

Fig. SEM images of (a) PP and (b) LDPE.

Fig. 2. Particle size distributions of PP and LDPE.

B. Experimental Procedures

Non-isothermal degradation experiments were carried out under ultra-high purity nitrogen atmosphere. Temperature range was from 298 to 1073 K. Nitrogen flow rate was maintained at 30 ml·min^{-1} and different heating rates used were 10, 15, 20 and 25 K·min^{-1}. Total sample mass was 4-5 mg for each run. In this work, the percent ratios of PP to LDPE were 100%:0%, 20%:80%, 35%:65%, 50%:50%, 65%:35%, 80%:20% and 0%:100%.

III. THEORY

Vyazovkin (VYZ) model-free method is started from rate equation and Arrhenius equation and based on an assumption that reaction model is independent on temperature and

heating rate [13]. The rate equation can be written as in (1):

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

where α is conversion, t is time, $k(T)$ is rate constant and $f(\alpha)$ is reaction model. The temperature dependence of $k(T)$ is described by the Arrhenius equation.

$$k(T) = A\exp\left(\frac{-E}{RT}\right) \tag{2}$$

where A and E are frequency factor and activation energy, respectively, and R is universal gas constant. Substitution of (2) into (1) gives:

$$\frac{d\alpha}{dt} = A\exp\frac{-E}{RT}f(\alpha) \tag{3}$$

For non-isothermal conditions, using chain rule, where:

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt}\cdot\frac{dt}{dT} \tag{4}$$

Equation (3) becomes:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(\frac{-E}{RT}\right)f(\alpha) \tag{5}$$

where $\beta = dT/dt$ is heating rate ($K\cdot min^{-1}$) and $d\alpha/dT$ is rate of conversion with respect to temperature (K^{-1}).

Integration of (5) gives:

$$g(\alpha) = \frac{A}{\beta}\int_0^{T_a}\exp\left(\frac{-E}{RT}\right)dT = \frac{A}{\beta}I(E,T_\alpha) \tag{6}$$

$g(\alpha)$ is an integral term of $f(\alpha)$, as written in (7).

$$g(\alpha) = \int_0^{\alpha}\left[f(\alpha)\right]^{-1}d\alpha \tag{7}$$

Since $f(\alpha)$ is independent of temperature and heating rate, this is likewise for its integral term. Hence, $\dfrac{I(E,T_a)}{\beta}$ is constant, where $I(E,T_\alpha)$ is a temperature integral and;

$$\int_0^{T_a}\exp\left(\frac{-E}{RT}\right)dT = I(E,T_\alpha) \tag{8}$$

For a set of four experiments, carried out at different heating rates (10, 15, 20 and 25 $K\cdot min^{-1}$), the activation energy can be determined at any particular value of α by finding the value of E_α, for which Ω function is minimum.

$$\Omega = \sum_{i=1}^n\sum_{j\neq 1}^n I\left(\frac{E_\alpha,T_{\alpha i}}{E_\alpha,T_{\alpha j}}\right)\frac{\beta_j}{\beta_i} \tag{9}$$

The temperature integral in (9) can be evaluated by several numerical approximation approaches. The typical one is the direct numerical integration method, when:

$$\int_0^{T_{\alpha i}}\exp\left(\frac{-E}{RT}\right)dT = \frac{E_\alpha}{R}P(u) \tag{10}$$

where E_α is the activation energy at each conversion, $T_{\alpha i}$ is

the temperature at each conversion for each heat rate, u is E_α/RT, and

$$P(u) = \int_u^{\infty}\frac{\exp(-u)}{u^2}du = \frac{\exp(-u)}{u} - E_i(u) \tag{11}$$

where $E_i(u) = \int_u^{\infty}\frac{\exp(-u)}{u^2}du$ and therefore:

$$I(E_\alpha,T_{\alpha i}) == \frac{E_\alpha}{R}\left[\frac{\exp(-u)}{u} - E_i(u)\right] \tag{12}$$

For Coats and Redfern approximation, the temperature integral term can be calculated using (13) [5].

$$I(E_\alpha,T_{\alpha i}) = \frac{RT_{\alpha i}^2}{E_\alpha}\left(1 - \frac{2RT_{\alpha i}}{E_\alpha}\right)\exp\left(\frac{-E_\alpha}{RT_{\alpha i}}\right) \tag{13}$$

For Gorbachev approximation, the temperature integral term can be calculated using (14) [5].

$$I(E_\alpha,T_{\alpha i}) = \frac{RT_{\alpha i}^2}{E_\alpha}\left(\frac{1}{1+\frac{2RT_{\alpha i}}{E_\alpha}}\right)\exp\left(\frac{-E_\alpha}{RT_{\alpha i}}\right) \tag{14}$$

For Agrawal and Sivasubramanian approximation, the temperature integral term can be calculated using (15) [5].

$$I(E_\alpha,T_{\alpha i}) = \frac{RT_{\alpha i}^2}{E_\alpha}\left(\frac{1 - \frac{2RT_{\alpha i}}{E_\alpha}}{1 - 5\left(\frac{RT_{\alpha i}}{E_\alpha}\right)^2}\right)\exp\left(\frac{-E_\alpha}{RT_{\alpha i}}\right) \tag{15}$$

For Cai *et al.*, approximation, the temperature integral term can be calculated using (16) [6].

$$I(E_\alpha,T_{\alpha i}) = \frac{RT_{\alpha i}^2}{E_\alpha}\left[\frac{E_\alpha/RT_{\alpha i} + 0.66691}{E_\alpha/RT_{\alpha i} + 2.64943}\right]\exp\left(\frac{-E_\alpha}{RT_{\alpha i}}\right) \tag{16}$$

IV. RESULTS AND DISCUSSIONS

A. Thermogravimetric Analysis of LDPE and PP

TG curves of LDPE and PP were shown in Fig. 3(a) and Fig. 4(a), respectively. Thermal degradation of PP occurred at a lower temperature range than that of LDPE due to non-stabilization effect of tertiary carbons during the thermal degradation of polymer chain. In addition, LDPE degradation was observed to be a single step, beginning at 600 K and ending at 750 K. Likewise, for PP degradation, the single step observation was also found and the degradation was begun at about 580 K and ended at 730 K. In addition, the variation of the temperature degradation range with respect to heating rate was also found. For all samples, the TG curves were shifted toward the higher degradation temperature range with increasing heating rate from 10 to 25 $K\cdot min^{-1}$. However, for PP (Fig. 3(a)), the shifting of the TG curves with increasing heat rate also tended to approach a limit value. Fig. 3(b) and Fig. 4(b) illustrated corresponding derivative thermogravimetric curves (DTG curves) of LDPE and PP,

respectively. It can be seen that maximum degradation rate of PP was higher than that of LDPE and its corresponding degradation temperature of PP was lower than that of LDPE. In addition, the maximum degradation rate and the degradation temperature at the maximum degradation rate (T_m) also increased with increasing heating rate and, for PP, this trend was found to approach the limit value. The possible explanation is because of a shorter soaking time at the higher heating rate and, hence, the actual sample temperature was in fact lower than a furnace temperature.

(a)

(b)
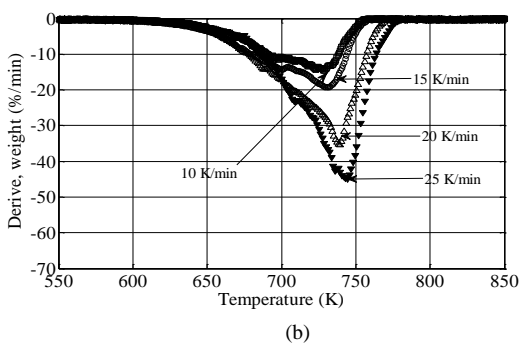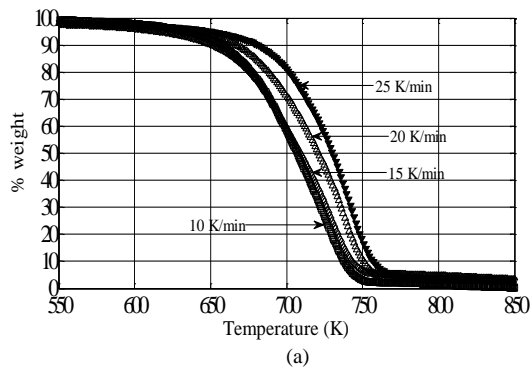
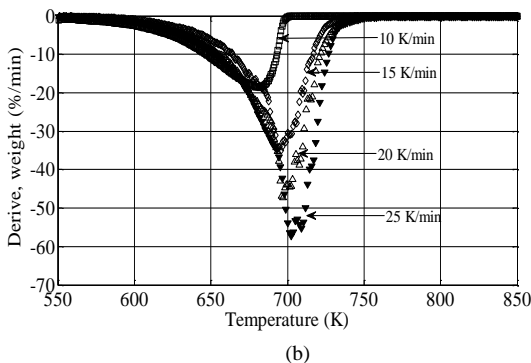Fig. 3. (a). TG and (b) DTG curves of LDPE.
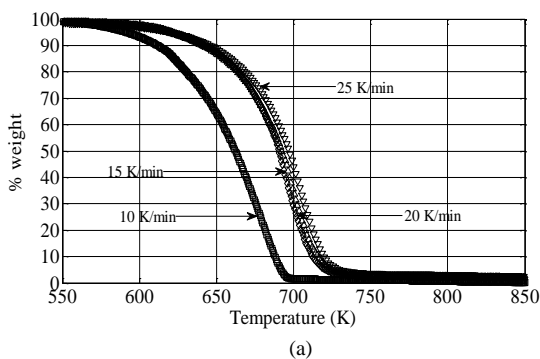

(a)

(b)

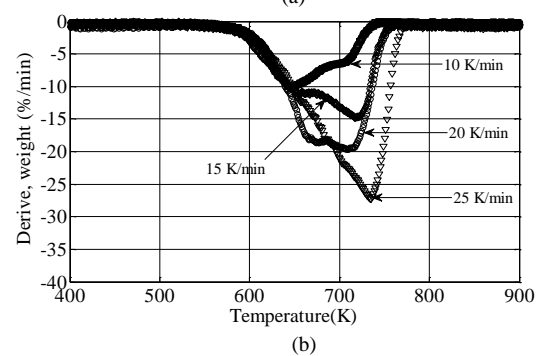Fig. 4. (a). TG and (b) DTG curves of PP.
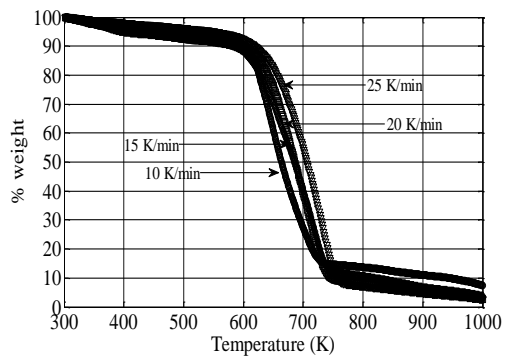

(a)

(b)

Fig. 5. (a). TG and (b) DTG curves of PP/LDPE mixture (PP/LDPE ratio = 20%:80%) at different heating rate.
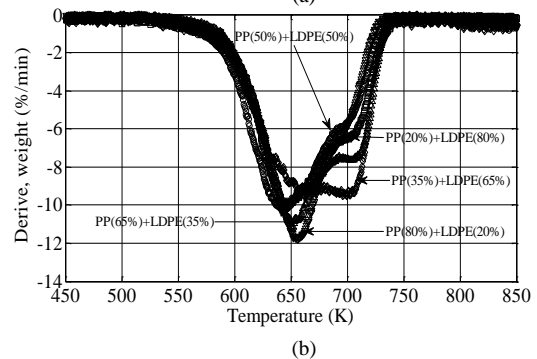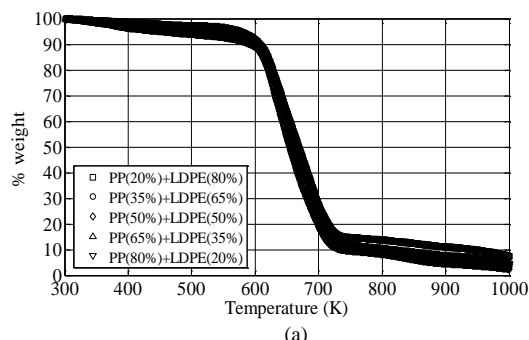

(a)

(b)

Fig. 6. (a). TG and (b) DTG curves of different PP/LDPE ratios at 10 K·min⁻¹.

B. Thermogravimetric Analysis of PP/LDPE Mixtures

The thermal degradation of PP/LDPE mixtures was also carried out for four heating rates (10, 15, 20 and 25 K·min⁻¹). The trend of the TG curves and the DTG curves of PP/LDPE mixtures (PP/LDPE ratio = 20%:80%) at the different heating rate was illustrated in Fig. 5. From Fig. 5(a), it can also be observed that the thermal degradation was a triple step process, where a beginning step was proximately at 350-600 K from $\alpha = 0.01$ to 0.1, an intermediate step was at 600-720 K from $\alpha=0.1$ to 0.9 and a final step was at 720-1000 K from $\alpha=0.9$-0.99. In addition, it was also found that the TG curves

were shifted toward the higher degradation temperature range with increasing heating rate. This was the same for all mixture compositions. For the effect of the heating rate on the maximum degradation rate and T_m, it was found from Fig. 5(b) that the maximum degradation rate and T_m increased with increasing heating rate. Considering Fig. 6, it can be seen that PP/LDPE compositions did not affect the TG curves (Fig. 6(a)) but the DTG curves (Fig. 6(b)). Considering DTG curve (Fig. 6(b)), in comparison with Fig. 3(b) and Fig. 4(b), the maximum degradation rates for the polyolefin mixtures were much less than that of the pure polymers. From TG and DTG curves (Fig. 6), in comparison with Fig. 3 and Fig. 4, boarder and lower ranges of the degradation temperature for the polyolefin mixtures than those of the pure polymers were found (see also Table I). From the TG and DTG curves of all PP/LDPE compositions, temperature at $\alpha = 0.01$ (T_d) and T_m were reported in Table I, as well as Fig. 7 for T_m and Fig. 8 for T_d for each heating rate. According to Fig. 7, it can be observed that, by adding PP in LDPE, T_m dropped from the value of 100% LDPE. Besides, with increasing a percentage of PP, the value tended to decreased further below T_m of 100%PP. This means the mixed polyolefin lowered T_m at the maximum degradation rate. In addition, T_m was also found to increase with increasing heating rate for the polyolefin mixture. For the change of T_d with the addition of PP, it can be observed from Fig. 8 that the T_d of the polyolefin mixture was lower than those of the pure polymers. However, with increasing percent PP, T_d tended to slightly increase. And the heating rate showed no clear effect on T_d.
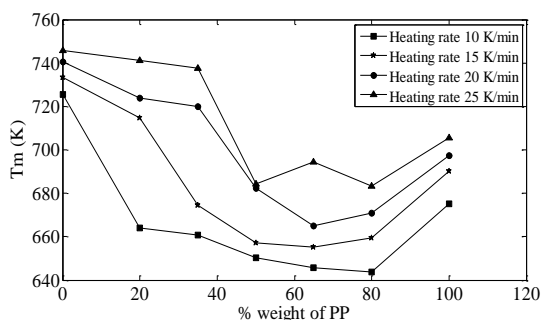

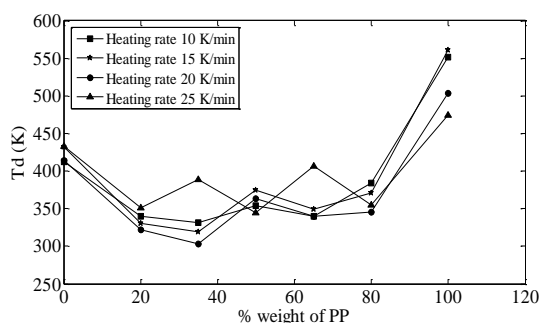Fig. 7. Variation of T_m with different PP/LDPE ratios at different heating rate.

Fig. 8. Variation T with different PP/LDPE ratios at different heating rate.

C. Kinetic Parameters Analysis for Thermal Degradation of Polyolefin Mixture

Following the calculation method concluded in the theoretical part, using different temperature integral approximation approaches, which were Coats and Redfern, Gorbachev, Agrawal and Sivasubramanian and Cai *et al.*

approximation, it can be observed that the different approximation approaches delivered the same values of the activation energy (Fig. 9 and Fig. 10). The same finding was also reported by Saha *et al.* [5]. Fig. 9 and Fig. 10 showed a dependency of the activation energy with respect to the conversion for LDPE and PP, respectively. From Fig. 9 and Fig. 10, it was pointed out that the activation energy of LDPE was higher than that of PP for the entire conversion range. It was also observed that, for LDPE (Fig. 9), the activation energy increased strongly with the conversion from the activation energy equal to 90-200 kJ/mole for the conversion equal to 0.1-0.8. Likewise, for PP (Fig. 10), the activation energy increased from 60 to 98 kJ/mole for the conversion equal to 0.2-0.7. A slightly different relation was found at the initial degradation process ($\alpha = 0.1$-0.2) and at the very end of the degradation process ($\alpha = 0.7$-0.8) where the activation energy was constant over these two conversion ranges.

TABLE I: DEGRADATION TEMPERATURE RANGE, T_D AND T_M OF POLYOLEFIN MIXTURE FROM TGA RESULTS

Plastics	Heating rate (K-min⁻¹)	Degradation temperature range (K) ($\alpha = 0.01$-0.99)	T_d/T_m(K)
PP(0%)+LDPE(100%)	10	412.1/814.5	412.1/725.6
	15	431.8/994.1	431.8/733.4
	20	414.5/968.8	414.5/740.5
	25	432.9/1004.7	432.9/745.7
PP(20%)+LDPE(80%)	10	339.4/1065.8	339.4/663.9
	15	330.4/1053.1	330.4/714.8
	20	321.7/1052.2	321.7/723.9
	25	351.0/1049.4	351.0/741.1
PP(35%)+LDPE(65%)	10	331.6/1054.5	331.6/660.6
	15	319.4/1045.4	319.4/674.5
	20	303.5/1052.4	303.5/720.1
	25	389.2/1036.9	389.2/737.6
PP(50%)+LDPE(50%)	10	353.9/1041.7	353.9/650.4
	15	374.8/1016.1	374.8/657.2
	20	363.4/1020.8	363.4/682.2
	25	344.7/1009.2	344.7/684.3
PP(65%)+LDPE(35%)	10	339.8/1061.2	339.8/645.6
	15	348.9/1056.8	348.9/655.3
	20	339.8/1058.2	339.8/664.9
	25	406.7/1045.8	406.7/694.5
PP(80%)+LDPE(20%)	10	384.3/1059.2	384.3/643.8
	15	370.6/1011.1	370.6/659.5
	20	345.7/1017.4	345.7/670.8
	25	355.0/1014.0	355.0/683.4
PP(100%)+LDPE(0%)	10	551.5/757.6	551.5/675.2
	15	560.7/995.3	560.7/690.3
	20	503.4/990.1	503.4/697.5
	25	474.4/995.4	474.4/705.4

Fig. 11 represented the relation between the activation energy and the conversion for PP/LDPE mixture at different PP/LDPE ratios (20%:80%, 35%:65%, 50%:50%, 65%:35% and 80%:20%). It can be approximated that, with increase fraction of PP, the activation energy decreased. In addition,

for all mixture compositions, it was found that the activation energy was slowly increased with the conversion during the initial degradation stage (α = 0.1-0.2). Then, the activation energy became nearly constant or a very weak function with the conversion during the middle stage of thermal degradation (α=0.2-0.6). It, finally, increased with increasing the conversion again during the final degradation stage (α=0.6-0.8). This finding was in contrast with the report of Chowlu *et al.* [11] who also studied the kinetic analysis of the non-isothermal degradation of PP/LDPE mixture. Based on VYZ model-free method and using direct numerical integration method instead of Cai *et al.* approximation approach for the temperature integral approximation, they reported that, the activation energy always increased with the conversion, where the gradual increase of the activation energy was found for the initial degradation process and the strong increase of the activation energy was found for the remaining degradation process.
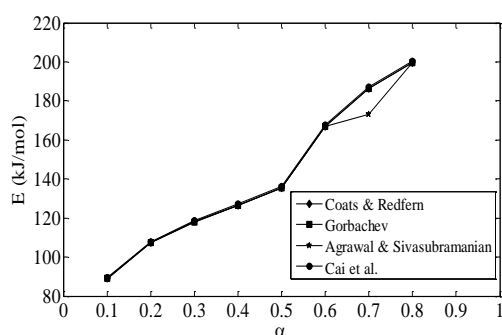

Fig. 9. Dependency of activation energy on conversion during non-isothermal degradation of LDPE using different temperature integral approximation approaches.
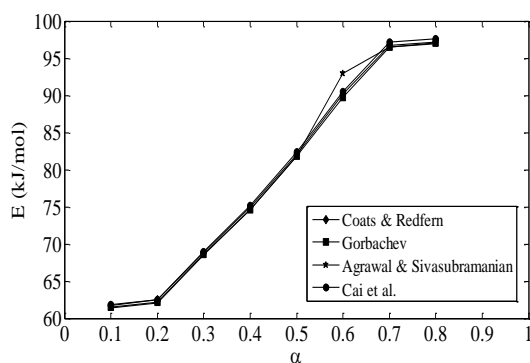

Fig. 10. Dependency of activation energy on conversion during non-isothermal degradation of PP using different temperature integral approximation approaches.
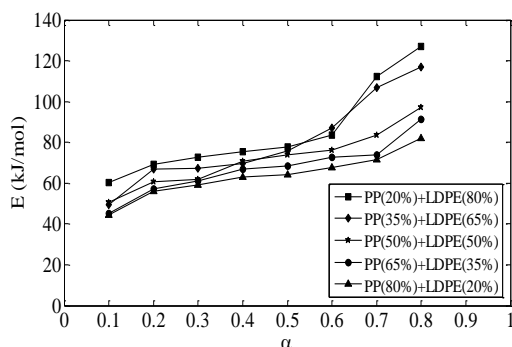

Fig. 11. Dependency of activation energy on conversion during non-isothermal degradtion of different PP/LDPE ratios using Cai *et al.* temperature integral approximation approach.

Another important point, which can be drawn from our work, was that the polyolefin mixture had the lower activation energy than those of the pure polymers (Fig. 11). The lowering in the activation energy for all mixtures compositions were corresponding to the lower degradation temperature, mentioned previously. This was also reported by Miranda *et al.* [14] that for the PP/PE mixture, PP caused a reduction of the activation energy. They explained in their work that free radicals were initially formed from the less stable polymer, which was PP in this case, due to a transfer of hydrogen. Then, these free radicals destabilized the more stable polymer (LDPE), resulting in the lower activation energy of the polyolefin mixture. And, the same explanation was also addressed by Chowlu *et al.* [11].

V. CONCLUSIONS

Kinetic analysis of thermal degradation of pure and mixed polyolefin under non-isothermal condition was carried out using thermogravimetric analysis (TGA) and Vyazovkin (VYZ) model-free method. It can be concluded that:

- TG curves of pure polyolefin followed a single step process but this was a triple step process for polyolefin mixture.
- Addition of percent PP lowered degradation temperature range, maximum degradation rate, degradation temperature at the maximum degradation rate and degradation temperature at conversion of 0.01, in comparison with those of the pure polymers.
- Different numerical temperature integral approximation approach showed no effect of the interpreted values of activation energy.
- The activation energy increased continuously with increasing conversion for pure LDPE. On the other hand, for PP, the activation energy increased with increasing conversion during an intermediate degradation stage, but was constant during an initial and a final degradation stage.
- For polyolefin mixture, with increasing conversion, the activation energy was increased during the initial degradation stage, constant during the intermediate degradation stage and increased again during the final degradation stage.
- The polyolefin mixtures had the lower activation energy than those of the original pure polymers. In addition, the activation energy decreased with increasing ratio of PP.

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