



Model-free Kinetic Analysis of Thermal Degradation of Polystyrene and High-Density Polyethylene Blends

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ABSTRACT

An objective of this work was to investigate kinetic information of a thermal degradation of polystyrene (PS) and high-density polyethylene (HDPE) blends under a pyrolysis atmosphere at different mixture compositions, using thermogravimetric analysis, operated non-isothermally, and model-free method. It was found that the degradation temperature range can be reduced by an addition of PS. This is probably due to an attack of PE by polystyryl radicals. With regard to an activation energy calculation based on model-free method, the activation energies of the thermal degradation tended to increase with a level of conversion, for all cases. The lower the level of conversion, the closer the activation energy value to that of 100%PS. With higher level of conversion, the activation energy values were approaching to that of 100% HDPE. This could be due to the fact that the polystyryl free radical from PS is diminished along the conversion path and, hence, at a higher level of conversion, the degradation process has no more influence of such free radical. Finally, the activation energy of single PS was lower than that of single HDPE and a proportion of PS to HDPE has no effect on the activation energy, but the level of conversion.

Keywords: thermal degradation, polystyrene, high-density polyethylene, model-free

1. INTRODUCTION

A chemical recycling method of polymer wastes through a thermal/catalytic degradation process under nitrogen atmosphere is the most beneficial method, because it can deliver many valuable products. In addition, it would be more useful if a particular attention is given to a management of the mixed polymer wastes rather than the single polymer, in particular the mixture between polyethylene and polystyrene (PS), which has been reported to

give a higher fraction of gasoline [1]. To the best of our knowledge, an important investigation on kinetic information of the thermal/catalytic degradation of polyolefin and polystyrene mixture is still insufficient and this information is a necessary for design and optimization of the pyrolytic equipment and process. Hence, scientific research in this particular area is a focus of this work.

Thermogravimetric analysis (TGA) is one of many techniques, used for the

investigation of the kinetics of the degradation of the polymers. The resulting percentage weight losses with respect to time or temperature, known as TG curves, can be used for the kinetic parameters interpretation.

The best calculation methods for the kinetic parameters from the TG curve is a model-free method. A feature of the model-free method is that, based on rate equation and Arrhenius equation, this method has no need for the presumed reaction model. To obtain the accurate activation energy, the TG data of the 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. Hence, it can help to reveal the complexity of multiple reactions due to the dependence of the activation energy on the extent of the conversion [2].

There are some previous works that have investigated the kinetics parameter of thermal degradation of polyolefin polymers with an application of the model-free method. [3] studied the thermal degradation kinetics of PET soft drink bottle waste using various temperature integral approximation approaches. The results showed the variation of the activation energy with the level of conversion, as well as the work of [4], who studied the thermal degradation kinetics of polyethylene (PE) waste and the work of [5], who studied the non-isothermal degradation of PP and LDPE blends of different ratios. In this later work, they also reported that the activation energy is much lower with the addition of PP. And, the ratio PP:LDPE of 80:20 is considered the most preferable composition because of its low activation energy and delivery of high amounts of light hydrocarbons ($\leq C_{10}$).

In this work, we investigated the kinetics of the thermal degradation of PS/HDPE

mixture at different mixture compositions under nitrogen atmosphere, using thermogravimetric analysis. Under the non-isothermal operation, the model-free method was used to interpret the kinetic parameters from the TG curves.

2. MATERIALS AND METHODS

2.1 Equipments and Materials

A thermogravimetric analyzer used in this work was Rigaku TGA (TG-DTA8120). The polymers used in this work were PS copolymer (Grade STYRON* 484H) and HDPE homopolymer (Grade HD2209J).

2.2 Sample Preparation Procedures

All the single polymers were shredded into powder form in the size range of 180-250 μ m. On the other hands, all the polymer blends were prepared by firstly weighing the polymers corresponding to the chosen percentage ratio before dissolving them in toluene solvent. The polymers were stirred thoroughly until the polymers were completely dissolved. The solution was firstly dried in an atmosphere so that almost all the toluene solvent was removed and the polymer blend was precipitated out. The polymer blend was placed in the vacuum oven at 50°C for 12 hours to completely remove all the toluene solvent. The polymer blend was further shredded and sieved to obtain the polymer blend in the size range of 180-250 μ m.

2.3 Experimental Procedures

Non-isothermal degradation experiments using the thermogravimetric analyzer were carried out under 99.99% purity nitrogen atmosphere. The temperature range was from 298 K to 1073 K. The nitrogen flow rate was maintained at 30 ml \times min⁻¹ and the different heating rates used were 10 K \times min⁻¹, 15 K \times min⁻¹, 20 K \times min⁻¹ and

25 K×min⁻¹. The total sample mass was 4-5 mg for each run. In this work, the percentage ratios of PS to HDPE were 100:0, 20:80, 35:65, 50:50, 65:35, 80:20 and 0:100.

3. THEORY

Model-free method [6, 7] commences by using rate equation and Arrhenius equation and is based on the assumption that the reaction model is independent of the temperature and heating rates. For non-isothermal conditions,

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (1)$$

where α is the conversion, T is the temperature, β is the heating rate, $f(\alpha)$ is the reaction model, A and E are the frequency factor and the activation energy, respectively, R is the universal gas constant. Integration of Eq. (1) gives

$$g(\alpha) = \frac{A}{\beta} \int_0^{T_\alpha} \exp\left(\frac{-E}{RT}\right) dT = \frac{A}{\beta} I(E, T_\alpha) = \int_0^\alpha [f(\alpha)]^{-1} d\alpha \quad (2)$$

$g(\alpha)$ is an integral term of $f(\alpha)$, $I(E, T_\alpha)$ is a temperature integral and T_α is a temperature at each conversion. Since $f(\alpha)$ is independent of temperature and heating rate, this is likewise for its integral term. Hence, $\frac{I(E, T_\alpha)}{\beta}$ is constant and;

$$\int_0^{T_\alpha} \exp\left(\frac{-E}{RT}\right) dT = I(E, T_\alpha) \quad (3)$$

For a set of four experiments, carried out at different heating rates, the activation energy can be determined at any particular value of α by finding the value of E_α (Activation energy at each conversion) for which the Ω function is the minimum:

$$\Omega = \sum_{i=1}^n \sum_{j \neq i}^n I\left(\frac{E_\alpha, T_{\alpha i}}{E_\alpha, T_{\alpha j}}\right) \frac{\beta_j}{\beta_i} \quad (4)$$

The temperature integral in Eq. (3) can be evaluated by several numerical approximation approaches. The typical one is the direct numerical integration method, by which

$$\int_0^{T_{\alpha i}} \exp\left(\frac{-E}{RT}\right) dT = \frac{E_\alpha}{R} P(u) \quad (5)$$

where u is E_α/RT , and

$$P(u) = \int_u^\infty \frac{\exp(-u)}{u^2} du = \frac{\exp(-u)}{u} - E_i(u) \quad (6)$$

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

$$I(E_\alpha, T_{\alpha i}) = \frac{E_\alpha}{R} \left[\frac{\exp(-u)}{u} - E_i(u) \right] \quad (7)$$

The temperature integral approximation approach used in this work was Cai *et al.* approximation (Eq. (8)) [4], which is one of the more accurate non-linear temperature integral approximations:

$$I(E_\alpha, T_{\alpha i}) = \frac{RT_{\alpha i}^2}{E_\alpha} \left(1 - \frac{2RT_{\alpha i}}{E_\alpha} \right) \exp\left(\frac{-E_\alpha}{RT_{\alpha i}}\right) \quad (8)$$

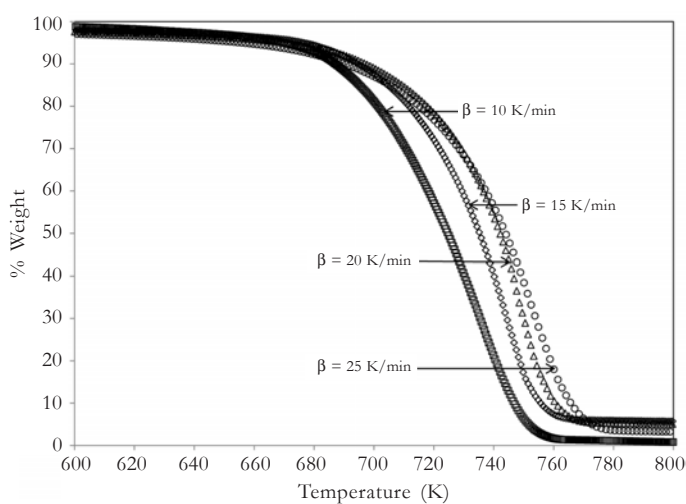
4. RESULTS AND DISCUSSION

4.1 Thermogravimetric Analysis of Thermal Degradation of 100%PS and 100%HDPE

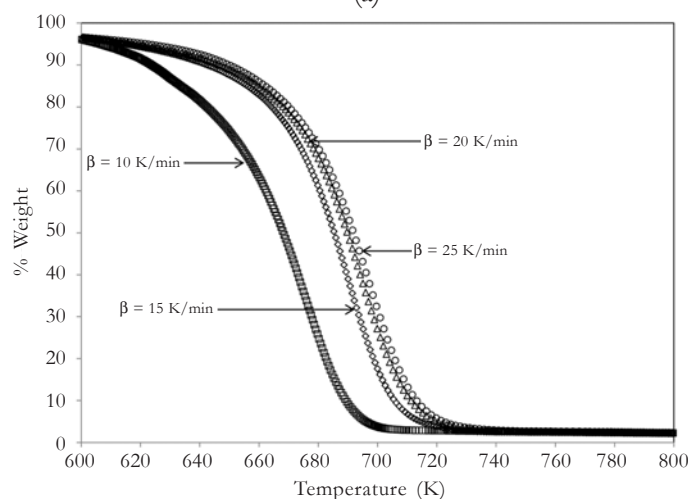
The TG curves of the thermal degradation of 100% PS and 100%HDPE are shown in figure 1(a) and figure 1(b), respectively. It can be observed that the thermal degradation of PS and HDPE was a single step process. In addition, the degradation temperature range for PS is lower than

that of HDPE. The explanation for this is basically due to bond energy analysis. For PS, there is a weak bond energy at tertiary carbons where the polystyryl radicals is bonded with the polymer main chain [1,8] Beside, it was also explained in [1] that there is a single C-H bond while carbon atoms at other positions along the main chain contain more than one C-H bonds. Since bond energy of C-H is 414 kJ/mole and the bond energy of C-C is 348 kJ/mole [9], as a result, the tertiary carbon position contains the

weakest bond energy and releases the polystyryl free radical. In comparison with HDPE, a straight polymer chain with high crystallinity resulted in a higher thermal stability. It can be seen also that the degradation temperatures shifted to higher ranges at higher heating rates. The possible explanation for this phenomenon is that it was because of the shorter soaking time at the higher heating rate and, hence, the actual sample temperature was in fact lower than a furnace temperature.



(a)



(b)

Figure 1. The TG curves at different heating rates of thermal degradation (a) 100%HDPE and (b) 100%PS.

4.2 Thermogravimetric Analysis of Thermal Degradation of PS and HDPE Blends

The TG curves of thermal degradation of PS/HDPE blends (PS:HDPE = 35:65) at 4 different heating rates is illustrated in figure 2. It can be observed that the thermal degradation of PS/HDPE blends was a triple step process. The first step is the gradual change of the percent weight from 100% to 90% in 300-650 K and is followed by the second step, where the major degradation process is occurred and the percent weight changes from 90 to 10% within 650-750 K. The final step is the change of the percent weight from 10%-0% in 750-1000K. For the PS/HDPE blends (table 1), the addition of PS reduced $T_{\alpha=0.10}$ and $T_{\alpha=0.90}$, where $T_{\alpha=0.10}$ is temperature at $\alpha = 0.10$ and $T_{\alpha=0.90}$ is temperature at $\alpha = 0.90$. However, the values were found to increase again at 100% PS.

Even the values of $T_{\alpha=0.10}$ and $T_{\alpha=0.90}$ were found to be lower than those of 100%PS and 100% HDPE, the major degradation temperature ranges of the blends were allocated within the ranges of 100% HDPE and 100%PS. And, it was illustrated that the higher the percentage PS, the lower the values of the major degradation temperature ranges (figure 3). Such a finding has not been reported before for the thermal degradation of the mixture between PS and HDPE. However, this can also be explained in the same fashion as that for the mixture between PP and LDPE, reported by [5]. As mentioned above, PS is a less stable polymer molecule in comparison with HDPE. With the polystyryl radicals, the degradation of the more stable polymer chain can be induced. As a consequence, the degradation temperature range of the PS/HDPE blends were found to be lower.

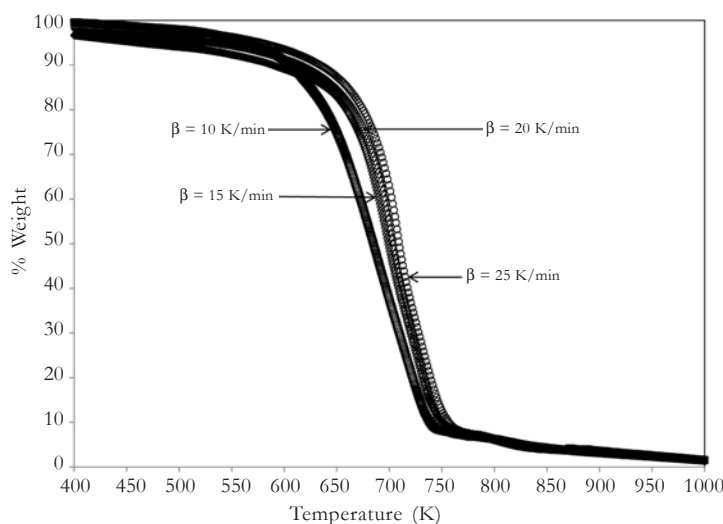


Figure 2. TG curve of PS to HDPE of 35 to 65 at different heating rates.

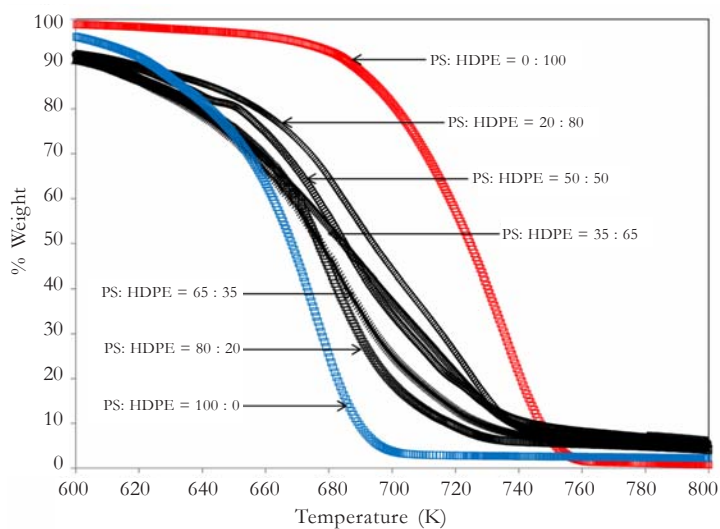


Figure 3. Comparison of TG curves at different PS:HDPE ratios (heating rate = 10 K/min).

4.3 Kinetic Parameter Analysis for Thermal Degradation of 100%PS and 100%HDPE

Figure 4 demonstrates the dependency of the activation energy with respect to conversion for the thermal degradation of PS and HDPE, respectively. It can be pointed out that the activation energy of HDPE was higher than that of PS for the entire conversion range. In addition, it can also be observed that for HDPE, the activation

energy decreased with the conversion from a value of the activation energy in the range of 180-230 kJ/mole for the conversion in the range of 0.14-0.44 and then increased with the conversion from 180-220 in the kJ/mole for the conversion in the range of 0.54-0.84. On the other hand, for PS, the activation energy increased from 80 kJ/mole to 135 kJ/mole for the conversion in the range of 0.14-0.34 and constant for the conversion from 0.34-0.84

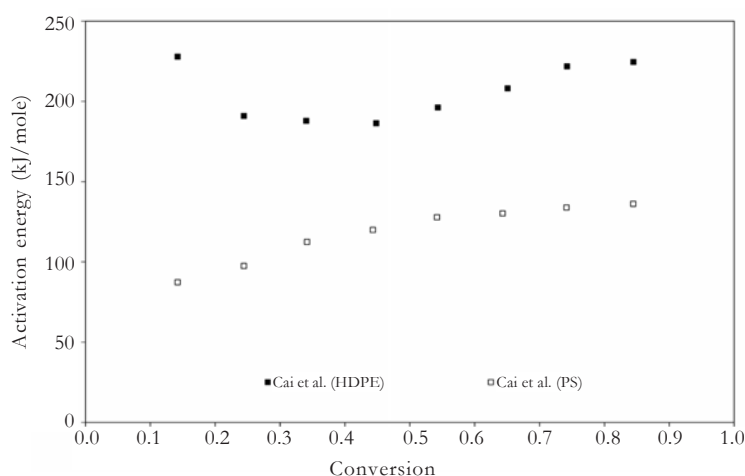


Figure 4. Variation of activation energy with respect to conversion for PS and HDPE.

Figure 5 showed the comparison between the activation energy of HDPE from previous works and our work. It was found that the values from this work was lower than those of [10] and [11], where the activation energy was found to be constant at approximately 296 kJ/mole.

Figure 6 showed a comparison of the activation energy from our work and previous research works, the activation

energy of PS from our work was found to be lower than those reported by [12], [13] and [14]. In addition, [12] and [14] reported at constant value at 200 kJ/mole. On the other hand, [13] reported a similar trend as our work but the higher values (100-200 kJ/mole). The explanation for the difference found was probably due to a different grade of polymer used or a different design of TGA itself causing a different TG curve obtained.

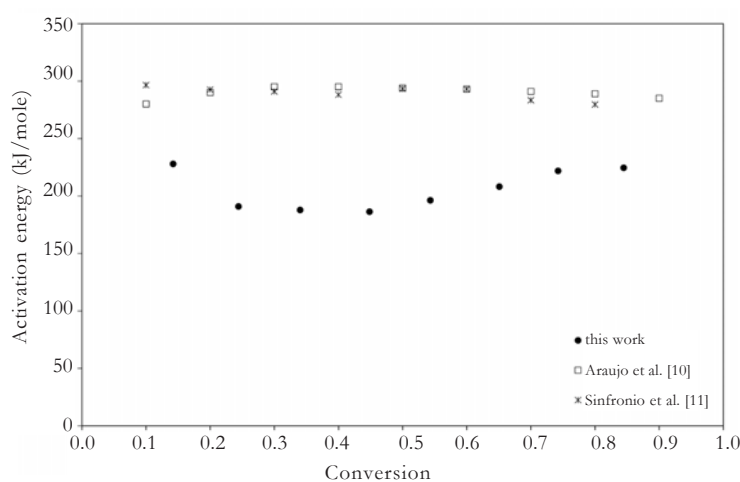


Figure 5. Comparison of activation energy of HDPE non-isothermal degradation from this work and previous research works.

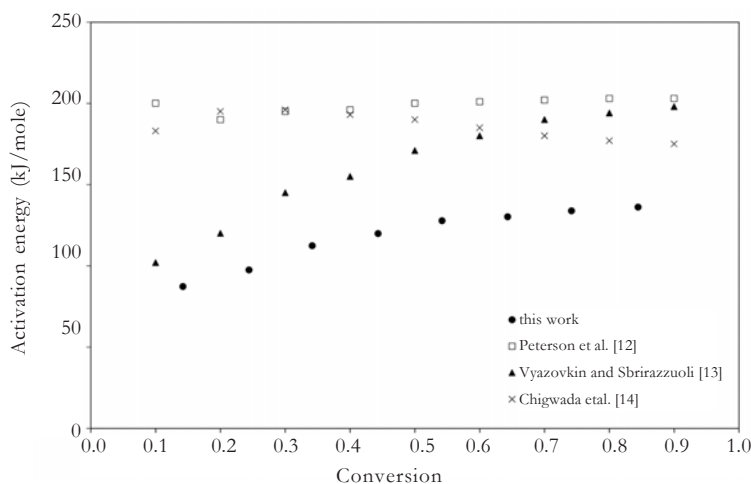


Figure 6. Comparison of activation energy of PS non-isothermal degradation from this work and previous research works.

4.4 Kinetic Parameter Analysis for Thermal Degradation of PS and HDPE Blends

Figure 7 presented the activation energy values at $\alpha=0.14$ for the polymer mixture at different mixture compositions. It can be observed that the mixture composition has no effect on the activation energy values and the same findings were found at different level of conversion. Figure 8 presents the relation between activation energy and conversion for the thermal degradation of the PS/HDPE mixture at different PS/HDPE percentage ratios (0:100, 20:80, 35:65, 50:50, 65:35, 80:20 and 100:0). It can be observed that the activation energies of the mixture are in between the values of 100%HDPE and 100%PS. In addition, it was observed that the values were increased with the level of conversion and the value was approached that of 100%HDPE at the higher

level of conversion. On the other hand, the lower the level of conversion, the closer the activation values to that of 100%PS. The similar trend was reported by [5], who also studied the kinetic analysis of the non-isothermal degradation of the PP/LDPE mixture. This is probably because the composition of reactants changes all along the conversion path and hence the reaction mechanism and the activation energy. At the lower level of conversion, there is probably higher content of polystyrene and its free radical. Therefore, the activation energy at the lower level of conversion is closer to that of PS. On the other hand, at the higher level of conversion, the temperature is higher and it is likely that there is lesser amount of polystyrene and its free radical is the system. As a result, the activation energy is approaching that of 100% HDPE at the higher level of conversion.

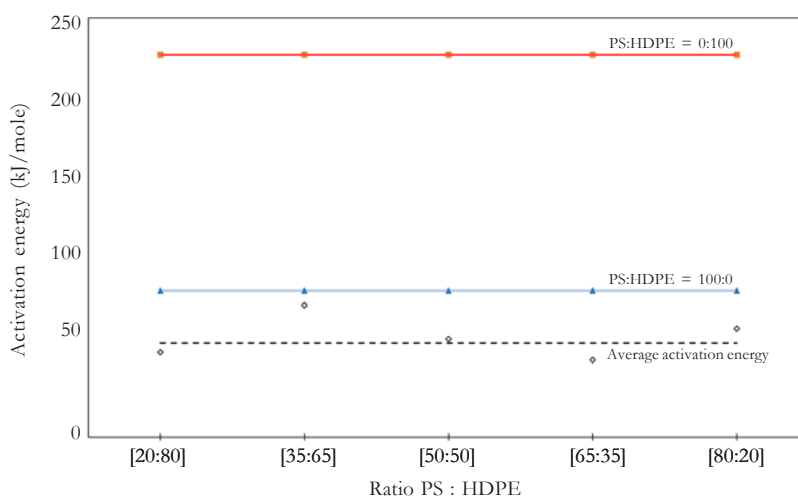


Figure 7. Activation energy of Polymer mixture of different mixture composition at $\alpha = 0.14$.

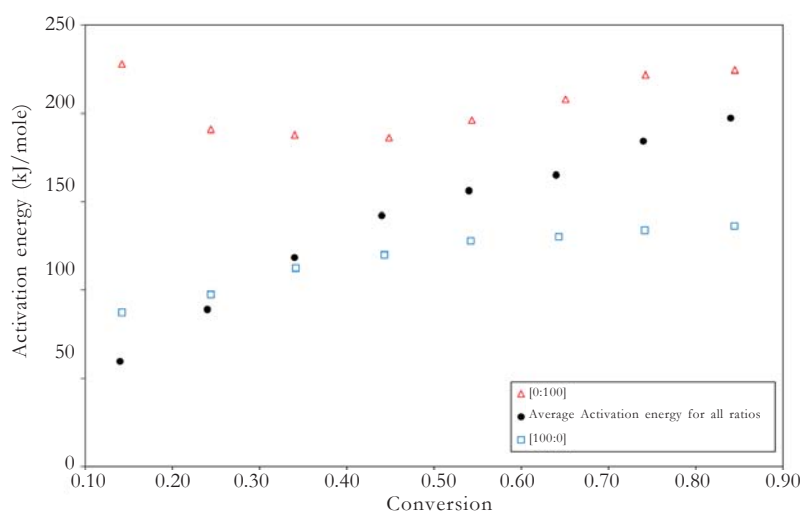


Figure 8. Activation energy of polymer mixture of different PS to HDPE ratio.

Table 1. $T_{\alpha=0.10} / T_{\alpha=0.90}$ of PS and HDPE mixture at different mixture composition at heating rate of 10 K/min.

PS:HDPE ratio	$T_{\alpha=0.10} / T_{\alpha=0.90}$ (K/K)
0:100	687.2/747.1
20:80	617.6/738.4
35:65	606.4/738.9
50:50	614.6/744.2
65:35	605.4/728.2
80:20	607.9/718.4
100:0	623.9/689.6

5. CONCLUSIONS

The kinetic analysis of the thermal degradation of polystyrene and high-density polyethylene blends under a nitrogen atmosphere and a non-isothermal condition was carried out using thermogravimetric analysis (TGA) and the model-free method. The kinetic information from this work has firstly provided a new insight on the thermal degradation of HDPE and PS polymer blend, which could be useful in the future as a specific data base for a design and configuration of the pyrolysis process of HDPE and PS polymer mixture to produce many valuable products.

It can be concluded that, from TG curves, a single step thermal degradation process was found for pure polymer, but a triple step process was found for polymer blends. In comparison between 100%PS and 100% HDPE, the temperature degradation ranges of 100%PS were always lower than those of 100%HDPE for all heating rates. In addition, the activation energies of 100% PS were always lower than those of 100%HDPE. However, it was found that for both polymers, the activation energy value increased with the level of conversion. This was also found for the case of the polymer blends, where the lower the level of conversion the closer the activation energy value to that of 100%PS and at the higher level of conversion the activation energy values were approaching to that of 100% HDPE. This could be due to the fact that the polystyryl free radical from PS is diminished along the conversion path and, hence, at higher level of conversion on, the degradation process has no more influence of such free radical. Finally, it was firstly pointed out from this work that the mixture composition has no effect on the activation energy values.

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