



## Pyrolytic decomposition and model-free kinetics analysis of mixture of polypropylene (PP) and low-density polyethylene (LDPE)

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### ABSTRACT

Thermal decomposition behaviour of mixtures of polypropylene (PP) and low-density polyethylene (LDPE) with different weight ratios (20:80, 35:65, 50:50, 65:35, 80:20) is studied under non-isothermal conditions at five different heating rates. Presence of synergistic effect is observed for mixture samples with PP composition >40 wt.%. Formation of hydrocarbons (<C<sub>6</sub>) and (C<sub>6</sub>–C<sub>10</sub>) fractions are the highest in case of (PP(65%) + LDPE(35%)). The nonlinear Vyazovkin model-free analysis is used to understand the variation of activation energy,  $E_{\alpha}$  with conversion,  $\alpha$ . For almost all the mixtures, initially  $E_{\alpha}$  is a slow but increasing function of  $\alpha$  and then becomes a very strong function of  $\alpha$  towards the end of the decomposition phenomenon.  $E_{\alpha}$  is much lower for the mixtures (PP(50%) + LDPE(50%)), (PP(65%) + LDPE(35%)) and (PP(80%) + LDPE(20%)). The plastic mixture PP:LDPE = 65:35% is the most preferable one during pyrolysis due to its low activation energy and formation of significantly high amount of hydrocarbons of range (<C<sub>10</sub>).

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### 1. Introduction

Disposal of polymer waste has become a big concern over the issue of environmental pollution. PE (polyethylene) and PP (polypropylene) are the most widely used commodity plastics [1]. PP being the most widely used commodity plastic has a major contribution (22%) of total thermoplastic materials produced in the World [2]. Hence, the kinetics of decomposition of PP and PE, which is an example of complex chain radical mechanism are of great interest [3]. Pyrolysis is considered as one of the reasonable and efficient means to dispose the waste, where the waste is converted into valuable products such as liquid and gaseous fuel. Both kinetics analysis and product distribution are essential parts to understand the exact reaction mechanism during pyrolysis. It is being reported that the yield of oil conversion is high in case of mixed plastic wastes [4]. Bockhorn et al. in their several papers [5–7] reported the stepwise pyrolysis of waste plastics mixtures. The kinetic data from stepwise pyrolysis of waste plastics containing PVC (polyvinyl chloride) confirmed that different molecular structures of commodity plastics brought about different reaction mechanisms of thermal decomposition, different reaction rates, and different temperature dependencies of the decomposition rates [7,8]. Presence of PVC in waste plastic mixture containing PE, PP, and PS (polystyrene) was

found to increase the formation of chloroorganic compounds in liquid fractions [9]. Faravelli et al. [10] observed some low reactivity of the PE polymers while in mixture form with PS, which was found to be due to the attack of the PS molecules while the degradation of PS is found to be independent of the presence of PE. They also reported that during deeper mixing the volatilization of PE increases, while depolymerization of the PS molecules occurs due to the attack of the PS radicals. Marcilla et al. [1] compared the catalytic degradation of polymer blends of PE and PP with thermal degradation experiments. They found that the weight loss behaviours of these polymers are quite sharp which depend on the heating rates. Ciliz et al. [11] carried out pyrolysis experiments on the mixtures of virgin and waste PP with waste PE and PS. When performed decomposition experiments on the mixtures of PP with PE and PP with PS polymers, they observed some marked differences in the weight loss behaviours due to the presence of impurities in the waste polymeric form. From the product analysis, they found that the gaseous content was increasing with the amount of PP in the mixture of PP and PE.

Thermogravimetric analysis (TGA) is reported to be one of the best techniques to study polymer decomposition kinetics [12]. Vyazovkin model-free technique [13–25] has become popular method in obtaining reliable and consistent kinetic information about the whole process of polymer decomposition. There have been several studies in recent times dealing with Vyazovkin model-free technique particularly for single plastics. In our previous publications we reported the model-free analysis of non-catalytic pyrolysis of polyethylene terephthalate (PET) [14], PE [23], catalytic pyroly-

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sis of LDPE (low density polyethylene) [24,25] over ZSM-5 and PP [26] along with the catalytic pyrolysis of PP over Al-MCM-41 [26]. The model-free kinetics analysis can provide information regarding possible reaction types. From the phenomenon of dependence of activation energy on the degree of reaction, the single-step or multi-step nature of reaction process can also be confirmed [27]. The dependence of activation energy on the extent of reaction enables us to detect the multi-step process and to conclude upon the polymer decomposition reaction mechanisms. More over, prediction of reaction kinetics over a wide temperature range is also possible by this method [28].

Thus, limited literatures are available on decomposition of plastic mixtures and their kinetics particularly using the model-free analysis. Therefore, in the present study, we have reported the thermal decomposition behaviour of mixture of PP and LDPE for various mixture compositions. We have studied the distribution of products coming out of such mixtures during decomposition. Further, we have used Vyazovkin model-free technique to understand the variation of activation energy with conversion. From the experimental decomposition data, product distribution and the information on activation energy we have analyzed the existence of interactions between the two polymers while undergoing the decomposition. We also have reported the best possible combination of the PE and PP samples in the mixture of the two during pyrolysis from the perspective of product distribution and activation energy.

## 2. Experimental

### 2.1. Materials

The non-catalytic non-isothermal decompositions were carried out for binary mixtures of PP and LDPE. PP (polypropylene homopolymer (PPHP), Trade name: Koylene ADL, Grade ASO30N) was supplied by Indian Petrochemicals, Vadodara, India with melt flow index 3.0 and LDPE. The PP sample used in this study has melting point: 175.69 °C, heat of fusion: 62.38 J g<sup>-1</sup> and percentage crystallinity: 32.83% [29]. The LDPE sample used in this study was used as computer cabinet and has melting point: 128.7 °C, heat of fusion: 38.37 J g<sup>-1</sup> and percentage crystallinity: 23.95% [24,29].

### 2.2. Thermal decomposition experiments for mixtures of PP and LDPE

Non-isothermal/dynamic thermogravimetric (TG) experiments were carried out in the TGA instrument, Mettler TOLEDO with model number TGA/SDTA 851<sup>e</sup> under nitrogen environment for a temperature range of 303–873 and 303–980 K. Nitrogen flow rate was maintained at 40–50 ml min<sup>-1</sup>. All samples were shredded into very small pieces (mesh size of 40/60). The samples mixtures of polymers (physical mixtures) were directly fed to the TGA instrument. The non-homogeneity of the mixture (if any) is neglected. Thermal decomposition experiments were carried out in dynamic condition at heating rates of 5, 10, 15, 20 and 25 K min<sup>-1</sup>. Platinum crucible (150 μL) was used as sample holder. Further details can be seen in our recent publications [14,23,24,26]. Experimental conditions for TGA studies are given in Table 1.

### 2.3. Product analysis using gas chromatograph

Product analysis studies were carried out using Varian 3800 Gas Chromatograph (GC). A gas-tight syringe (Hamilton, gas-tight, model no. 1005, 5 ml) was used for the injection of evolved gases from the TGA at maximum decomposition temperature,  $T_m$ . Gas chromatographic separation was performed on a mild-polarity column, VF-200ms (30 m length, 0.25-μm film thickness, 0.25 mm ID) composed of 100% trifluoropropyl methyl siloxane phase. A

constant helium flow of 1.0 ml min<sup>-1</sup> with 1:50 split ratio was maintained during the product analysis. The oven temperature was programmed as heating to 323 K and hold for 2 min. Then ramp heating at a rate of 6 K min<sup>-1</sup> to 573 K and hold for 15 min. Standardization of gas samples were carried out using standard samples such as pure propane gas supplied by Vadilal Gases Ltd.; n-hexane, heptane, benzene, and toluene supplied by Merck, India; indene, naphthalene, bi-phenyl, and fluorine supplied by Ranbaxy Laboratories Ltd., India were also injected maintaining the similar condition as to analyze their retention times.

## 3. Kinetics analysis

The kinetics model equation combined with the Arrhenius approach of the temperature function of reaction rate constant is expressed as

$$\frac{d\alpha}{dt} = k_0 \exp(-E_\alpha/RT)f(\alpha) \quad (1)$$

where  $t$  is time (min),  $T$  is temperature (K),  $\alpha$  is conversion of reaction  $(W_0 - W)/(W_0 - W_\infty)$ ,  $W_0$ , initial weight of the sample (mg),  $W$  is sample weight (mg) at any temperature  $T$ ,  $W_\infty$ , final sample weight (mg),  $d\alpha/dt$  is rate of reaction (min<sup>-1</sup>), and  $f(\alpha)$ , reaction model.  $k_0$  is the pre-exponential factor (K<sup>-1</sup>) and  $E_\alpha$ , the activation energy (kJ mol<sup>-1</sup>) are the Arrhenius parameters.  $R$  is the gas constant (kJ mol<sup>-1</sup> K<sup>-1</sup>). At a constant heating rate under non-isothermal conditions Eq. (1) can be written as

$$\beta \frac{d\alpha}{dT} = k_0 \exp(-E_\alpha/RT)f(\alpha) \quad (2)$$

where  $\beta = dT/dt$  is the heating rate (K min<sup>-1</sup>) and  $d\alpha/dT$  is rate of reaction (K<sup>-1</sup>).

For a given conversion and a set of  $n$  experiments carried out at different heating rates  $\beta_i$  ( $i = 1, \dots, n$ ). The activation energy, ( $E_\alpha$ ) can be determined at any particular value of  $\alpha$  by finding the value of  $E_\alpha$  for which the objective function  $\Omega(E_\alpha)$  is minimized [16–19], where

$$\Omega(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{I(E_\alpha, T_{\alpha,i}) \beta_j}{I(E_\alpha, T_{\alpha,j}) \beta_i} \quad (3)$$

Using experimental values of  $T_\alpha$  and  $\beta$  and minimizing the function  $\Omega(E_\alpha)$ , the value of the  $E_\alpha$  is obtained at a given conversion. The objective function,  $\Omega(E_\alpha)$  minimization is done by numerical method in MATLAB using 'medium-scale: Quasi-Newton line search' algorithm. The 'fminunc' function for unconstrained problem is applied for the optimization [14,23,24,26].

Where

$$I(E_\alpha, T_{\alpha,i}) = \int_0^{T_{\alpha,i}} \exp\left(\frac{-E_\alpha}{RT}\right) dT \quad (4)$$

The temperature integral is evaluated by direct numerical integration, where the temperature integral takes the form

$$I(E_\alpha, T_{\alpha,i}) = \int_0^{T_{\alpha,i}} \exp\left(\frac{-E_\alpha}{RT}\right) dT = \frac{E_\alpha}{R} \left[ \frac{\exp(-u)}{(u)} - Ei(u) \right] \quad (5)$$

where,

$$u = \frac{E_\alpha}{RT} \quad \text{and} \quad Ei(u) = \int_u^\infty \frac{\exp(-u)}{u} du \quad (6)$$

**Table 1**  
Non-isothermal experimental condition of TGA studies for polymer samples.

Sample	Initial mass (mg)	Heating rate (K min <sup>-1</sup> )	Temperature range (K)	% Residue	T <sub>d</sub> /T <sub>m</sub> (K)
PP [26]	19.77	5	303–873	1.49	596.9/706.8
	20.32	10	303–873	0.88	670.0/723.1
	20.67	15	303–873	0.51	684.6/731.4
	19.78	20	303–873	0.73	684.8/736.8
	19.41	25	303–873	0.70	696.6/742.9
PP(20%) + LDPE(80%)	9.23	5	303–980	2.21	549.6/722.9
	10.01	10	303–980	1.86	574.0/731.1
	9.36	15	303–980	2.14	578.3/744.0
	8.6	20	303–980	1.73	556.1/748.7
	10.03	25	303–980	1.76	573.9/753.6
PP(35%) + LDPE(65%)	7.248	5	303–980	2.38	567.0/715.7
	7.96	10	303–980	1.94	574.2/727.8
	8.14	15	303–980	1.98	589.0/735.3
	8.185	20	303–980	1.52	581.2/741.2
	7.94	25	303–980	1.69	566.1/744.5
PP(50%) + LDPE(50%)	8.01	5	303–980	2.79	567.0/687.5
	8.67	10	303–980	1.87	592.1/713.7
	8.53	15	303–980	1.83	596.2/718.3
	12.32	20	303–980	1.63	603.7/738.9
	9.5	25	303–980	1.51	577.5/738.8
PP(65%) + LDPE(35%)	10.98	5	303–980	1.26	576.0/677.5
	8.72	10	303–980	2.18	593.4/705.4
	8.63	15	303–980	1.79	589.2/719.0
	10.45	20	303–980	0.81	596.3/730.5
	10.5	25	303–980	1.44	607.8/737.0
PP(80%) + LDPE(20%)	10.76	5	303–980	1.23	575.9/681.1
	10.68	10	303–980	1.65	595.7/701.2
	11.17	15	303–980	1.28	596.4/722.1
	10.89	20	303–980	1.27	615.4/729.1
	10.84	25	303–980	1.24	615.3/738.6
LDPE [24]	7.77	5	303–980	3.17	633.0/734.2
	8.45	10	303–980	1.55	640.2/741.4
	11.19	15	303–980	2.29	654.0/754.0
	8.68	20	303–980	2.68	665.0/763.2
	10.91	25	303–980	2.79	686.1/770.4

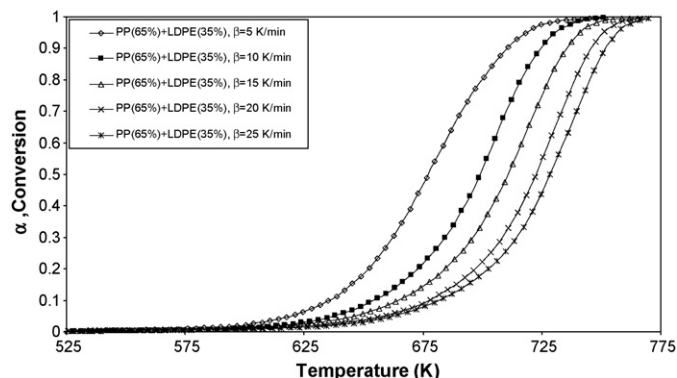
Detailed development of Eq. (5), numerical procedure, and algorithms for model-free technique are discussed in our recent publication [23,24,26].

## 4. Results and discussion

### 4.1. Non-isothermal decomposition at several heating rates

Dynamic thermal decomposition of the PP and LDPE mixture samples was carried out at five different heating rates (5, 10, 15, 20, and 25 K min<sup>-1</sup>). Earlier, we have reported the results of thermal decomposition of pure LDPE [24] and pure PP [26,30]. However, the temperature at which  $\alpha \approx 0.01$  ( $T_d$ ) and the temperature at which the maximum weight loss rate occurs ( $T_m$ ) are reported in Table 1 for each case of experiments. It is observed that like the pure LDPE [24] and pure PP [26,30] both the thermogravimetric (TG) curves and derivative thermogravimetric (DTG) curves for the different compositions of the LDPE and PP mixtures also show constant pattern behaviour at different heating rates. Sample plots for variations of conversion (TG) and rate of conversions (DTG) for LDPE:PP (35%:65%) sample at different heating rates are shown through Figs. 1 and 2 respectively. The shift of the TG and DTG (Figs. 1 and 2) curves with heating rate is progressive and approaching towards a limit [30]. In the polymer categories under PE group, the higher the branching degree the lower the density, and lower the decomposition temperature [1]. Therefore, PP as expected decomposes at much lower temperature than LDPE. Accordingly, the maximum

decomposition temperatures,  $T_m$  observed for LDPE and PP at 10 K min<sup>-1</sup> are 741.4 and 723.1 K respectively (Table 1). But though expected,  $T_m$  for the different mixtures does not lie in between the above two temperatures. Fig. 3 indicates variation of  $T_m$  with variation of the mixture compositions. From Fig. 3 as well as Table 1, the observed trend in the variation of  $T_m$  for different polymer samples of PP and LDPE is LDPE > (PP(20%) + LDPE(80%)) > (PP(35%) + LDPE(65%)) > PP > (PP(50%) + LDPE(50%)) > (PP(65%) + LDPE(35%)) > (PP(80%) + LDPE(20%)). It can be observed from the trend of the figure (Fig. 3) that for mixture samples with PP composition >40%,



**Fig. 1.** Variation of conversion ( $\alpha$ ) with temperature during pyrolysis of polymer sample (PP:LDPE = 65%:35%) at different heating rates.

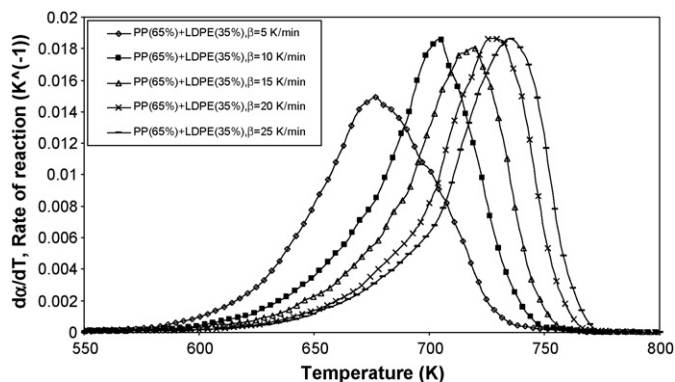


Fig. 2. Variation of rate of conversion ( $d\alpha/dT$ ) with temperature during pyrolysis of polymer sample (PP:LDPE = 65%:35%) at different heating rates.

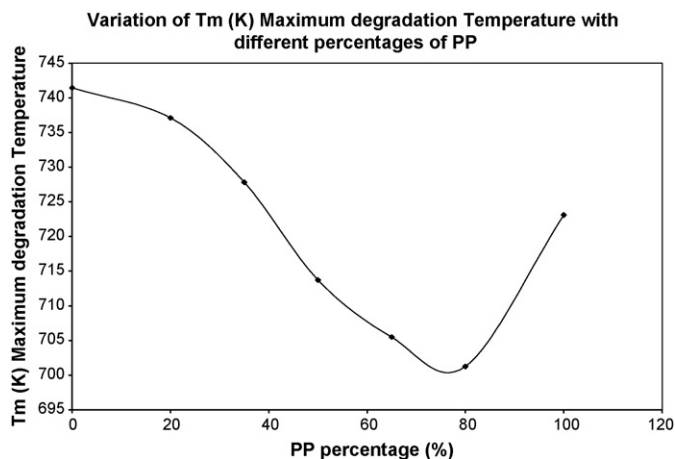


Fig. 3. Variation of maximum decomposition temperature,  $T_m$  for different percentages of PP at  $10 \text{ K min}^{-1}$  heating rate.

values of the  $T_m$  lies even below the  $T_m$  of pure PP sample, the lower maximum decomposition temperature of the two. The reason could be the Synergistic Effect during the decomposition of LDPE and PP mixture where an intermolecular transfer of a hydrogen atom takes place from the less stable polymer to a free radical depropagating chain of the second component during decomposition [31]. Figs. 4 and 5 showing the sample TG and DTG curves respectively at  $10 \text{ K min}^{-1}$  for the different compositions of the mixtures further illustrate the presence of interaction between the polymers during thermal decomposition of the mixtures. Ciliz et al. [11] during decomposition exper-

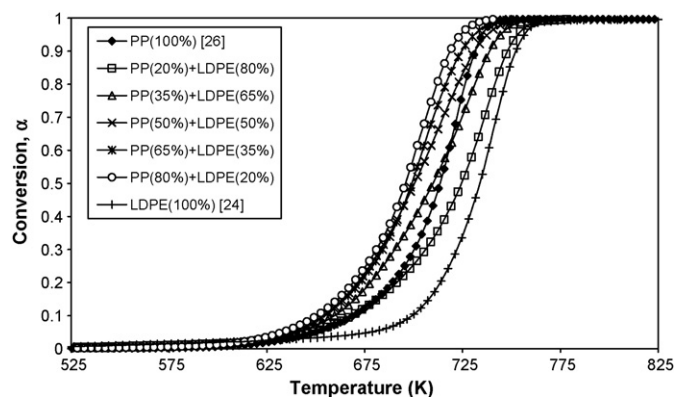


Fig. 4. Variation of conversion ( $\alpha$ ) with temperature during thermal pyrolysis of different polymer samples at  $10 \text{ K min}^{-1}$ .

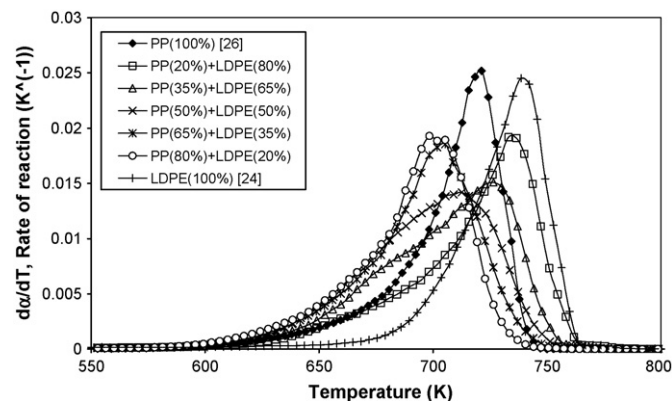


Fig. 5. Variation of rate of decomposition ( $d\alpha/dT$ ) with temperature during thermal pyrolysis of different polymer samples at  $10 \text{ K min}^{-1}$ .

iments on the mixtures of PP and PE observed some marked differences in the weight loss behaviours due to the interaction between the polymers. Similar phenomenon is also observed in the present study as obvious from Figs. 4 and 5. It is observed that for the pyrolysis of both the samples (PP(50%) + LDPE(50%)) and (PP(65%) + LDPE(35%)), till 695 K conversion,  $\alpha$  is about 0.43 (Fig. 4) but majority of the decomposition of (PP(65%) + LDPE(35%)) is completed quite earlier than (PP(50%) + LDPE(50%)) (Fig. 5). The comparison in Fig. 4 shows that for PP(100%) at  $T_m = 723.1 \text{ K}$  conversion,  $\alpha$  is about 0.74, for (PP(80%) + LDPE(20%)) at  $T_m = 701.2 \text{ K}$ ,  $\alpha$  is about 0.62, for (PP(65%) + LDPE(35%)) at  $T_m = 705.4 \text{ K}$ ,  $\alpha$  is about 0.61, for (PP(50%) + LDPE(50%)) at  $T_m = 713.7 \text{ K}$ ,  $\alpha$  is about 0.67, for (PP(35%) + LDPE(65%)) at  $T_m = 727.8 \text{ K}$ ,  $\alpha$  is about 0.74, for (PP(20%) + LDPE(80%)) at  $T_m = 731.1 \text{ K}$ ,  $\alpha$  is about 0.61 and for LDPE(100%) at  $T_m = 741.4 \text{ K}$ ,  $\alpha$  is about 0.67. Thus, from this observation it is found that in terms of conversion,  $\alpha$  at the respective  $T_m$  the following trend is followed by the polymer samples undergoing decomposition  $\text{PP} \approx (\text{PP}(35\%) + \text{LDPE}(65\%)) > (\text{PP}(50\%) + \text{LDPE}(50\%)) \approx \text{LDPE} > (\text{PP}(80\%) + \text{LDPE}(20\%)) \approx (\text{PP}(65\%) + \text{LDPE}(35\%)) \approx (\text{PP}(20\%) + \text{LDPE}(80\%))$ . It can be observed from Fig. 5 that maximum rates of decomposition for the polymer mixtures are much less and continue for a wider range of temperatures with broader peaks than that of the single polymer samples. This is also an indication of the presence of interactions between the polymer samples. The interaction effect is further illustrated in the subsequent section from the product distribution which is a complex phenomena for PP compared to LDPE [3].

#### 4.2. Product analysis

In the present work we have performed product distribution studies of various mixtures of PP and LDPE as well as the individual polymers using GC. Fig. 6 shows the comparison of gaseous products evolved at around  $T_m$  of thermal degradation of the polymer mixtures of PP and LDPE. The figure shows that the presence of lower hydrocarbons ( $<C_6$ ) with retention time less than 10 min is significantly high (52.5%) in case of (PP(65%) + LDPE(35%)) and fair in case of (PP(80%) + LDPE(20%)) followed by (PP(20%) + LDPE(80%)). This fraction of hydrocarbons is considerably less in case of the other polymer samples used.

In case of the gasoline range ( $C_6$ – $C_{10}$ ) fraction, the gaseous products obtained from the thermal decomposition of (PP(65%) + LDPE(35%)) again emerged to be the highest one (around 22.55%). This fraction is comparatively less in case of the gaseous products obtained from the sample (PP(80%) + LDPE(20%)) where yield is around 11.17%. But for other polymer samples the ( $C_6$ – $C_{10}$ ) fraction is significantly less.

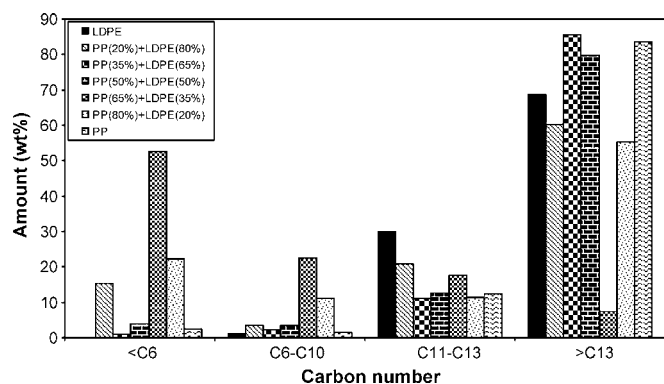


Fig. 6. Comparison of carbon number distribution of the gaseous products obtained at  $T_m$  of different polymer samples.

In case of the yield of hydrocarbons in the range of  $C_{11}$ – $C_{13}$  for the different mixtures are pretty close and the following trend is observed  $LDPE > (PP(20\%) + LDPE(80\%)) > (PP(65\%) + LDPE(35\%)) > (PP(50\%) + LDPE(50\%)) > PP > (PP(80\%) + LDPE(20\%)) > (PP(35\%) + LDPE(65\%))$ .

The yield of higher hydrocarbons beyond  $C_{13}$  increases in all the polymer samples and polymer blend samples except  $(PP(65\%) + LDPE(35\%))$ . The yield of this fraction (beyond  $C_{13}$ ) follows the following trend:  $(PP(35\%) + LDPE(65\%)) > PP > (PP(50\%) + LDPE(50\%)) > LDPE > (PP(20\%) + LDPE(80\%)) > (PP(80\%) + LDPE(20\%)) > (PP(65\%) + LDPE(35\%))$ .

Other compounds such as indene ( $C_9$ ), naphthalene ( $C_{10}$ ); biphenyl ( $C_{12}$ ) and fluorene ( $C_{13}$ ) are also detected in trace quantities from the degradation of the polymer samples.

According to Fig. 6, formation of heavier fractions gradually increases for samples PP, LDPE,  $(PP(35\%) + LDPE(65\%))$  and  $(PP(50\%) + LDPE(50\%))$ . For the samples  $(PP(80\%) + LDPE(20\%))$  and  $(PP(20\%) + LDPE(80\%))$ , initially a decrease and then again increase of heavier fraction is observed. For sample  $(PP(65\%) + LDPE(35\%))$ , there is a gradual decrease in formation of the heavier hydrocarbons.

According to the literature [32], at the very first step melting of the polymers take place and thereafter the thermal degradation of polyolefins undergoes the sequence: chain radical mechanism  $\rightarrow$  initiation  $\rightarrow$  H-abstraction  $\rightarrow$   $\beta$ -scission  $\rightarrow$  radical recombination. According to Westerhout et al. [33] one of the most important steps of thermal degradation is  $\beta$ -scission, which has important influence on the product distribution during polymer degradation. Increased occurrence of  $\beta$ -scission increases the yield of  $C_2$  products. It is also pointed out in the literature [11,34,35] that presence of PP in the mixture of PP and PE increases production of higher volatile products. Similar results are also observed in the present case for some of the mixture samples (Fig. 6).

According to the literature [36], LDPE and PP are incompatible in the melt and the blend exists as a two-phase mixture. The phase boundary is different for different compositions of the mixture. As PP degrades at lower temperature than PE [34,37], initially radicals from PP are formed in case of the mixture. These radicals then migrate towards the PP/PE boundary and interact with PE and accelerate the degradation of PE but PE has a stabilizing effect on PP [31,37]. Therefore, different product distribution is possible at different compositions. It is worth mentioning here that the product distribution reported in the present study is as observed at the respective maximum decomposition temperature ( $T_m$ ) of the polymer samples which are different for different compositions. According to Lee and Shin [38], the mixture can show different degradation mechanisms at different temperatures leading to the formation of different products.

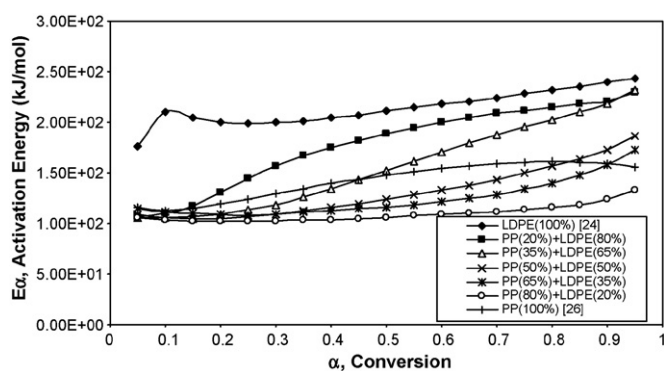


Fig. 7. Dependency of activation energy on conversion during thermal decomposition of different polymer samples.

However, from the very high yield of lower hydrocarbons ( $<C_6$ ) for the mixture  $(PP(65\%) + LDPE(35\%))$ , it can be concluded that  $PP:LDPE = 65\%:35\%$  is the most preferred choice of mixture composition when lighter hydrocarbon products are desired. However, the product distribution pattern in case of the mixtures of PP with LDPE is quite complex and possibly indicative of interactions between the polymers at certain stages of degradation and at certain temperatures. Further studies in this regard are needed to conclude upon exact nature of the interaction that takes place at different temperatures for different mixture compositions.

#### 4.3. Model-free analysis for PP and LDPE decomposition

Dependency of activation energy,  $E_\alpha$  on conversion,  $\alpha$ , for non-isothermal decomposition of the mixture polymers and the pure PP and LDPE are presented through Fig. 7. Variations of  $E_\alpha$  with  $\alpha$  for individual PP and individual LDPE samples have been discussed in our recent publications [24–26]. However, for almost for all the mixtures it is found that initially  $E_\alpha$  is a slowly increasing function of  $\alpha$  and then becomes a very strong function of  $\alpha$  towards the end of the decomposition phenomenon (Fig. 7). It is also found that activation energy is highest for the decomposition of the waste LDPE sample and much lower for the mixtures  $(PP(50\%) + LDPE(50\%))$ ,  $(PP(65\%) + LDPE(35\%))$  and  $(PP(80\%) + LDPE(20\%))$ . The lower activation energies for the above three mixtures is also evident from the very low values of their  $T_m$ .

Thus the above study reveals that the composition  $PP:LDPE = 65\%:35\%$  is the most preferable one during pyrolysis of the polymer mixture due to its low activation energy and formation of significantly high amount of the lower hydrocarbons.

## 5. Conclusion

Thermal degradation study on binary mixtures of PP and LDPE with different weight ratios (20:80, 35:65, 50:50, 65:35, 80:20) have been carried out. The TG and DTG curves with heating rate are progressive and approaching towards a limit and the trend is similar for the different mixture compositions. Presence of synergistic effect is anticipated for all the mixture compositions and is prominent for mixture samples with PP composition  $>40$  wt.% when the values of the  $T_m$  lies even below the maximum decomposition temperature of the less thermally stable polymer, PP in the present case. From the comparison of gaseous products evolved at around  $T_m$  of thermal degradation of the polymer mixtures, it is observed that presence of hydrocarbons ( $<C_6$ ) and ( $C_6$ – $C_{10}$ ) fractions are the highest in case of  $(PP(65\%) + LDPE(35\%))$  and fair in case of  $(PP(80\%) + LDPE(20\%))$ . The yield of higher hydrocarbons beyond  $C_{13}$  increases in all the polymer samples and polymer mixtures except  $(PP(65\%) + LDPE(35\%))$ . The complex nature of the product distribution pattern in case

of the mixtures of PP with LDPE is indicative of possible interactions between the polymers at certain stages of degradation and at certain temperatures. This observation demands further studies to examine the exact nature of the interaction taking place at different temperatures for different mixture compositions. For almost all the mixtures, initially  $E_{\alpha}$  is a slow but increasing function of  $\alpha$  and then becomes a very strong function of  $\alpha$  towards the end of the decomposition phenomenon.  $E_{\alpha}$  is much lower for the mixtures (PP(50%) + LDPE(50%)), (PP(65%) + LDPE(35%)) and (PP(80%) + LDPE(20%)) compared to other compositions. Finally, the plastic mixture PP:LDPE = 65%:35% is the most preferable one during pyrolysis due to its low activation energy and formation of significantly high amount of the hydrocarbons of range ( $\leq C_{10}$ ).

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