# THERMOGRAVIMETRIC CHARACTERISTICS AND KINETIC OF CO-PYROLYSIS OF OLIVE RESIDUE WITH HIGH DENSITY POLYETHYLENE

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The co-pyrolytic behaviour of olive residue/high-desity polyethylene mixture was examined with a thermogravimetric analyser. The experiments were done over the temperature range of room temperature to 1273 K at various heating rates (2, 10, 20 and 50 K min$^{-1}$) and in a nitrogen atmosphere.

The results indicated that mass loss process of mixture consists of three distinct stages and the increase of the heating rate shifts in the maximum rate loss to higher temperature. The difference of mass loss ($\Delta m$) between experimental and theoretical, calculated as algebraic sums of the mixture for different heating rates of 2, 10, 20 and 50 K min$^{-1}$, is about 7–11% at 740–900 K. These experimental results indicate a significant synergistic effect during co-pyrolysis of olive residue with high-density polyethylene. In addition, a kinetic analysis was performed to fit thermogravimetric data, the mixture is considered as multi-stage process. A reasonable fit to the experimental data was obtained for all materials and their mixture by isoconversional Friedman method.

## Introduction

Over the past decades, the use of plastics has become increasingly common in developing countries; methods to dispose of plastic waste, however, have not developed significantly in these countries. Plastic waste is usually dumped together with organic waste. With the increasing need for energy, the increasing dependency on fossil fuels, and the growing depletion of petroleum reserves, the call for more sustainable solutions becomes louder.

Co-pyrolytic techniques have received much attention in recent years because they provide an alternative way to dispose and convert polyolefins and cellulose (or lignin) derived materials into high value feedstock and the specific benefits of this method potentially include: the reduction of the volume of waste; the recovery of chemicals and the replacement of fossil fuels.

Biomass fuels are composed of biopolymers that consist of various types of cells and the cell walls are built of cellulose, hemicelluloses and lignin. Cellulose and hemicelluloses form mainly volatile products during pyrolysis due to the thermal cleavage of the sugar units. The lignin forms mainly char since it is not readily cleaved to lower molecular mass fragments [1, 2].

Polyolefinic polymers, like polyethylene and polypropylene, contain approximately 14 mass% hydrogen. These materials could provide hydrogen during thermal co-processing with biomass and can lead to an increase of liquid production.

Thermogravimetric analysis is one of the most common techniques used to investigate thermal events and kinetics during thermal degradation of oil shale and plastic [3–5]. The thermal decomposition of biomass derived materials has been studied [6, 7]. Two peaks that appear in thermogravimetric curves are due to hemicellulose (the first one) and cellulose (the second one), whereas lignin decomposes in a broad range of temperatures. Numerous studies on the thermal decomposition of polyolefin and, in particular, polyethylene have been carried out, especially in inert atmosphere [8, 9]. Polyolefinic materials such as high density polyethylene show a different behaviour to lignocellulosic materials. Under pyrolysis conditions, the material decomposition starts at approximately 673 K and progresses very rapidly up to 723–743 K without producing solid residue that could be used as combustible for supplying energy to the global process.

Several studies have been devoted to the study of the thermal decomposition of mixtures of polymers and lignocellulosic materials [10–14].

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Sharypov *et al.*[ 10] examined the combination of biomass with synthetic polymer mixtures and reported that biomass is thermal degraded at a lower temperature than the polyolefin and independent thermal behaviours were observed for each component of biomass/plastic mixtures. Jakab *et al.* [11, 12] analysed the effect of the presence of cellulose derivatives on thermal decomposition of vinyl polymers. The presence of lignocellulosic materials slightly affects high-density polyethylene decomposition, as the main degradation processes of cellulose derivatives have ended before high-density polyethylene begins to degrade. On the other hand, the effect of the presence of polypropylene on the thermal decomposition of cellulose derivatives was negligible. When degradation of biomass and polystyrene mixtures was evaluated, the yield of monomer, dimer and trimer from polystyrene decomposition was reduced, indicating that the radical chain reactions and intramolecular hydrogen transfer reactions were hindered by the presence of lignocellulose char [11]. In some cases, the polymeric matrix can influence the thermal degradation of cellulosic materials. Matsuzawa *et al.* [13] reported that poly(vinyl chloride) (PVC) and poly(vinylidene chloride) (PVdC) may affect the cellulose thermal degradation. HCl evolution in the dehydrochlorination reaction of vinyl chlorides seems to act as acid-catalyst to promote the dehydration reaction rather than the depolymerization reaction in cellulose pyrolysis. Similar results for mixtures of different kind of paper and vinyl polymers were reported by Sorum *et al.* [14]. However, and in spite of the above mentioned studies, there is a lack of information about the influence of cellulosic materials on the thermal degradation of polymers. The analysis of the thermal behaviour of mixtures of lignocellulosic materials and polymers is important not only from the recycling but also from the processing point of view. During processing, cellulose components produce a significant amount of char as the result of thermal degradation, which may affect the pyrolysis of the polymer as in the case of polyolefin [12].

Interactions between polymers and biomass are not well known. The main goal of this paper is to evaluate the interaction between olive residue (OR) and high-density polyethylene (HDPE) during pyrolysis. Thermal analysis of pure components and mixture was performed by thermogravimetric analyser under dynamic conditions. The calculation of apparent activation energies was based on the application of the isoconversional Friedman method [15].

## Experimental

### *Materials and samples preparation*

ORs (mixture of all solid components) were obtained from Marrakech area which located about 300 km of Rabat. Olive residues were obtained from the solid product of traditional olive oil process (Maâsra in Morocco). Air-dried olive residues were ground to obtain a uniform material of an average particle size (0.2 mm). The chemical composition of the olive residues are given in Table 1.

**Table 1** Chemical composition of OR

| Biopolymer composition | Mass% |
|---|---|
| Cellulose | 27.3 |
| Hemicellulose | 32.7 |
| Lignin | 33.8 |
| Holocellulose | 60.0 |
| Extractives | 60.2 |

The samples of HDPE were provided by Plador (Marrakech, Morocco). The OR:HDPE (1:1 mass ratio) mixture was blended by tumbling for 30 min in order to achieve homogeneity. In all experiments, samples of around 20 mg with particle sizes ranging approximately from 0.1 and 0.2 mm were placed in the platinum crucible of a thermobalance.

### *Experimental techniques*

OR, HDPE and their mixture samples were subjected to thermogravimetric analysis in a nitrogen atmosphere. Rheometrix Scientific STA 1500 TGA analyzer was used to measure and record the sample mass change with temperature over the course of the pyrolysis reaction. Thermogravimetric curves were obtained at four different heating rates (2, 10, 20 and 50 K min$^{-1}$) between 300 and 1275 K; the precision of reported temperatures was estimated to be ±2°C. Nitrogen gas was used as an inert purge gas to displace air in the pyrolysis zone, thus avoiding unwanted oxidation of the sample. A flow rate of around 60 mL min$^{-1}$ was fed to the system from a point below the sample and a purge time of 60 min (to be sure the air was eliminated from the system and the atmosphere is inert). The balance can hold a maximum of 45 mg; therefore, all sample amounts used in this study averaged approximately 20 mg. The reproducibility of the experiments is acceptable and the experimental data presented in this paper corresponding to the different operating conditions are the mean values of runs carried out two or three times.

**Table 2** Different temperature values of the OR, HDPE and their mixture

| Sample | Heating rate/K min$^{-1}$ | First step/K $T_1/T_{max}/T_F$ | Second step/K $T_1/T_{max}/T_F$ | Third step/K $T_1/T_{max}/T_F$ |
|---|---|---|---|---|
| Olive residue | 2 | 430/499/537 | 537/558/608 | |
| | 10 | 447/543/572 | 572/600/622 | |
| | 20 | 453/562/587 | 587/611/644 | |
| | 50 | 463/576/602 | 602/623/662 | |
| HDPE | 2 | 654/728/751 | | |
| | 10 | 694/757/784 | | |
| | 20 | 713/761/801 | | |
| | 50 | 718/779/854 | | |
| Olive residue/HDPE | 2 | 431/506/535 | 535/570/607 | 652/734/743 |
| | 10 | 455/546/580 | 580/598/633 | 695/766/788 |
| | 20 | 460/565/590 | 590/613/650 | 708/774/802 |
| | 50 | 472/577/607 | 607/630/680 | 726/794/832 |

## Results and discussion

### Thermal degradation of olive residue

Figure 1 shows the TG/DTG curves at four different heating rates of 2, 10, 20 and 50 K min$^{-1}$ from room temperature to 975 K. Table 2 shows the temperatures of the start ($T_I$) and finish ($T_F$) of the main mass loss, the temperatures of maximum rate of mass loss for the two main peaks of the DTG curves and the intermediate temperatures for all the heating rates.

The TG curves showed a slight mass loss occurring from ambient temperature to about 420 K due to the loss of water present in the material and external water bounded by surface tension. The thermal degradation of OR starts at approximately 450 K, and there follows a major loss of mass where the main devolatilization occurs and is essentially complete by approximately 660 K. This is followed by a slow further loss of mass until 970 K, after which there is essentially no further loss of mass. The residual mass amounted around of 19–24% and was decreased when the heating rate increased.

In the DTG curves, there are clearly two overlapping peaks and as the heating rate was increased, the two peaks become progressively merged. The composition of the biomass was cellulose, hemicellulose, lignin and extraneous components and the thermal degradation of individual components has been to extrapolate to the overall degradation of the original biomass [16]. In the thermal degradation of OR, the lower temperature peak was mainly represented by the decomposition of hemicellulose, and the higher temperature peak was mainly represented by cellulose. The peak corresponding of lignin is overlapping by the other
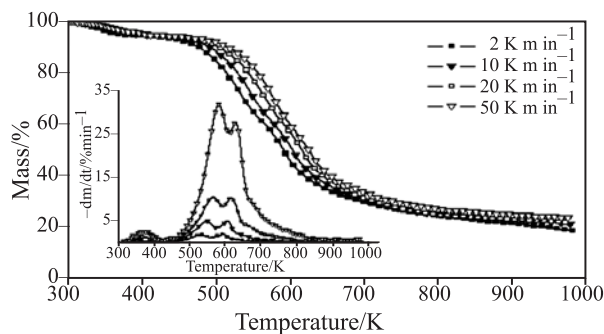


**Fig. 1** TG curves of OR at different heating rates. Inset: corresponding DTG curves

two peaks; lignin decomposes slowly over a very broad range of temperatures, providing a gently sloping baseline [7]. It appears that the second peak is a prolongation of the first peak. This point is in accordance with the idea that lignin begins to decompose at low temperatures (similar to those at which hemicellulose begins to decompose) but its range of thermal decomposition extends to higher temperatures.

Table 2 shows that there was a lateral shift to higher temperatures $T_{max1}$ and $T_{max2}$ for OR as the heating rate was increased. The lateral shift is also illustrated in Fig. 1. The lateral shift has been reported for different types of biomass [16–18] and has been assigned as being due to the combined effects of the heat transfer at different heating rates and the kinetics of the decomposition resulting in delayed decomposition.

### Thermal degradation of HDPE

TG and DTG curves of thermal decomposition of HDPE at four heating rates are represented in Fig. 2.
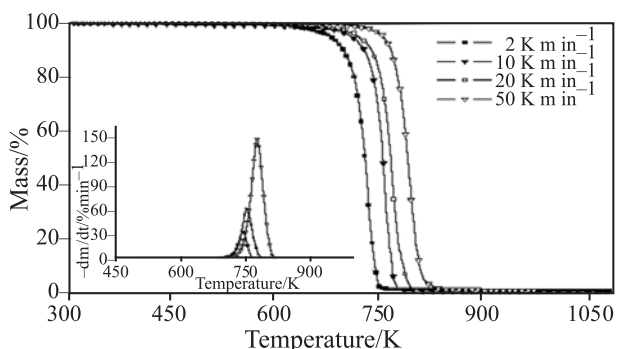
**Fig. 2** TG curves of HDPE at different heating rates. Inset: corresponding DTG curves

It can be seen that the shape of the mass curves does not change with variations in heating rate, but mass loss temperatures show an increase at higher heating rates. The mass loss shows that degradation occurs almost totally in one step as can be concluded by the presence of only one peak in DTG.

The TG curves show that the HDPE thermal degradation starts at 654 K and is almost complete at approximately 854 K. At higher heating rate the maximum degradation rate shifted from 728 K at 2 K min$^{-1}$ to 779 K at 50 K min$^{-1}$. The maximum degradation rate also increased from 7.37% min$^{-1}$ at 2 K min$^{-1}$ to 140.25% min$^{-1}$ at 50 K min$^{-1}$. The TG/DTG curves were displaced to higher temperature due to the heat transfer large with increasing heating rate. The characteristic temperatures are summarized in Table 2.

*Thermal degradation of the mixture*

The TG/DTG curves of mixture of OR and HDPE at heating rates of 2, 10, 20 and 50 K min$^{-1}$ are presented in Fig. 3. The main phenomena characterizing the degradation of the separate components appear also in the mixture. It can be seen that the decomposition of OR is almost completed before the beginning of that corre-
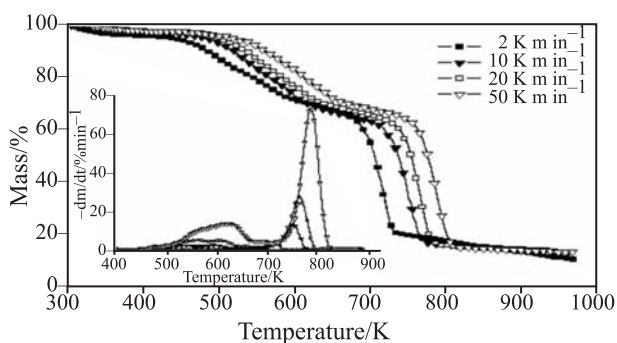
sponding to HDPE. It should be added that the residue yield of the mixture is lower than that of OR alone.

The TG/DTG curves show clearly three steps. The first step, obtained in the temperature range (431–607 K), is attributed to the decomposition of hemicelluloses. The second step occurs between 535 and 680 K, which corresponds to the decomposition of cellulose. The third step between 652 and 832 K was attributed to the decomposition of HDPE and lignin in the mixture. Some differences in such temperatures are observed when compared to those of pure materials. HDPE significantly increases its maximum temperature (6–15°C), while the variations for OR are less pronounced (1–5°C), but both materials increase their thermal stability.

To investigate whether interactions existed between OR and HDPE, we defined the difference of mass loss ($\Delta m = m_{mixture} - (x_1 m_1 + x_2 m_2)$), where $w_{mixture}$ is the mass loss of mixture, $x_i$ is the mass fraction of each material in the mixture and $w_i$ is the mass loss of each material in the same operational conditions. Obviously, $\Delta m$ describes the 'extent' of synergistic effect during pyrolysis of olive residue mixed with HDPE in Fig. 4. The difference of mass loss ($\Delta m$) between experimental and theoretical, calculated as algebraic sums of the mixture for different heating rates of 2, 10, 20 and 50 K min$^{-1}$, is about 7–11% at 740–900 K. These experimental results indicate a significant synergistic effect during co-pyrolysis of OR with HDPE. At 10 K min$^{-1}$, the mixture exhibits more evident synergistic effect in our experiments.

As can be seen in Fig. 3, the decomposition curves of both components are partially overlapped, therefore some kind of solid–solid or solid–gas interaction must be considered. Since OR thermal degradation occurs at lower temperature than HDPE, two main interactions can be assumed: in the solid state, between the char produced during OR degradation and HDPE; and solid–gas, between HDPE and the gaseous products evolved from OR degradation. In the solid state, hydrogen type
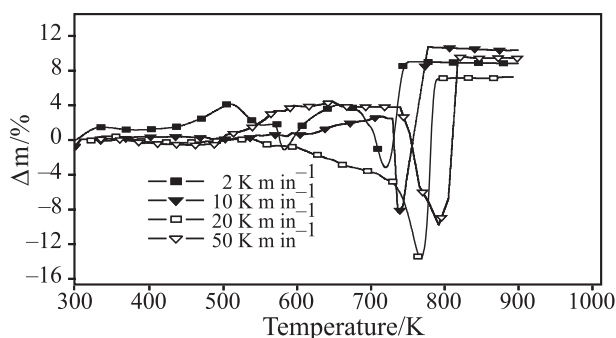


**Fig. 3** TG curves of mixture at different heating rates. Inset: corresponding DTG curves



**Fig. 4** Variation of $\Delta m$ for HDPE and OR mixture at different heating rates

interactions may occur between the OR and HDPE. These interactions delay the OR dehydration reaction, which takes place at lower temperatures than depolymerisation. As degradation proceeds, the effect of hydrogen interactions decreases, but char and gases evolved from OR degradation (mainly $CO_2$, CO and aldehydes) may interact with solid HDPE. On the other hand, char formed during OR degradation may act as a thermal stabiliser for HDPE. Thus, the increment in the thermal stability may be a consequence of the presence of strong interactions between both co-components in the solid state. The formation of char as a decomposition product of OR may be the main cause of the changes in HDPE degradation processes.

The obtained results are in good agreement with those of Jakab et al. [11]. It was shown that the char issued biomass shifts to a higher temperature of the thermal degradation of polyethylene, but the product distribution does not change substantially. This effect is explained by the influence of the char on the radical degradation mechanism of the polyethylene.

*Determination of kinetic parameters*

The kinetics of thermal decomposition reactions of carbonaceous materials is complex, in that decomposition of carbonaceous materials involves a large number of reactions in parallel and in series. Although thermogravimetry provides general information on the overall reaction kinetics, rather than individual reactions, it could be used as a tool for providing comparison of kinetic data of various reaction parameters such as temperature and heating rate. So the biomass and plastic pyrolysis reaction equation may simply be expressed as the following formula:

$$\frac{dx}{dt} = A\exp\left(-\frac{E}{RT}\right)f(x) \qquad (1)$$

where $A$ is pre-exponential factor, $E$ is activation energy, $T$ is temperature, $t$ is time, $f(x)$ is function of conversion. $x$ is pyrolysis conversion.

The Friedman method [15] was adopted in this work for the kinetic analysis of the thermogravimetric
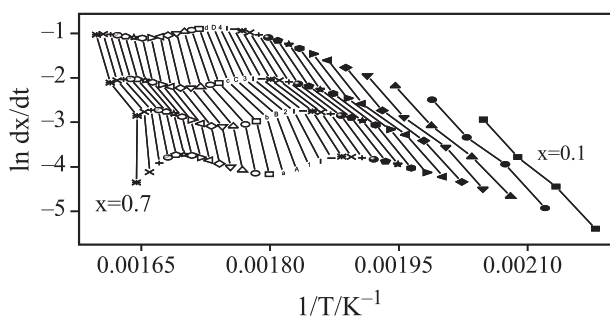
curves of these materials. This method is directly based on Eq. (1) whose logarithm is

$$\ln\left(\frac{dx}{dt}\right) = \ln[Af(x)] - \frac{E}{RT} \qquad (2)$$

Plotting $\ln(dx/dt)$ *vs.* $1/T$ at a given conversion yield a straight line of slope $-E/R$.

Isoconversional Friedman plots obtained for OR are shown in Fig. 5, where two regions can be clearly identified. It is assumed that the first process ($0.08<x<0.4$) corresponds to the hemicellulose degradation, while the second one ($0.52<x<0.72$) corresponds to the cellulose degradation. As the lignin degradation process is observed for a wide range of $x$, it is not considered in the $E_a$ calculation as well as those values in the transition region ($0.4<x<0.52$). The average $E_a$ calculated in such way for the first region was 165 kJ mol$^{-1}$, while $E_a$ for the second region was 219 kJ mol$^{-1}$. These results seem to confirm the existence of two different processes in the olive residue thermal degradation. Garcia Perez et al. analysed the thermal degradation of sugarcane bagasse, a lignocellulosic derivative [6]. The global pyrolysis of sugarcane bagasse was assumed to be the sum of the contribution of each component (hemicellulose, cellulose and lignin), and they used an algorithm to predict the kinetic parameters as the best fitting to the proposed equation. $E_a$ values found by them were 105 and 235 kJ mol$^{-1}$ for hemicellulose and cellulose respectively.
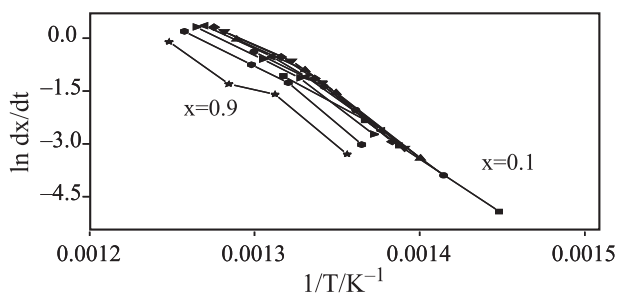


**Fig. 6** Friedman plots for HDPE thermal degradation



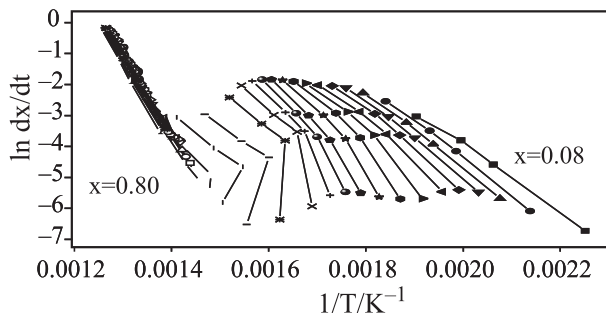**Fig. 5** Friedman plots for OR thermal degradation



**Fig. 7** Friedman plots for OR:HDPE (1:1) thermal degradation

A similar study was carried out for the HDPE. Figure 6 shows the isoconversional Friedman plots for HDPE. From the slopes, the average $E_a$ for $0.1 < x < 0.9$ was 247 kJ mol$^{-1}$. $E_a$ values do not change significantly with conversion (as can be concluded from the slopes in Fig. 5). The calculated apparent activation energies reported in the literature for HDPE varied over a wide range. Aguado *et al.* [19] reported activation energy of HDPE degradation ($260 \pm 23$ kJ mol$^{-1}$), Sorum *et al.* [14] found for HDPE degradation activation energy of 445 kJ mol$^{-1}$. Wu *et al.* [20] used thermogravimetry to study pyrolysis of plastic mixtures of MSW, the apparent activation energy of HDPE degradation was found of 233 kJ mol$^{-1}$.

Friedman method was also applied to the study of thermal degradation of the OR:HDPE 1:1 mixture. The isoconversional Friedman plots are shown in Fig. 7. It is possible to take three different regions corresponding to both degradation processes. $E_a$ calculated with this method was 155 kJ mol$^{-1}$ for the first region, 212 kJ mol$^{-1}$ for the second region and 220 kJ mol$^{-1}$ for the third process. When comparing these results with those of the pure materials, it is easy to note that the presence of HDPE does not significantly change the apparent activation energy of thermal decomposition of OR (with in the error of the method), but the $E$ value for HDPE in the mixture was somewhat lower than for the pure material.

Thermal degradation of cellulosic materials was recently studied [6, 12, 17]. Cellulose degradation proceeds by two competing reactions: dehydration and depolymerisation. The first reaction progresses by forming char, $CO_2$, CO, $H_2O$ and other volatiles (i.e. aldehydes) with intra-ring scission of the glucose unit in cellulose chains [11]. The second reaction is initiated by depolymerisation at high temperature producing $CO_2$, CO, liquid products and char. These products may influence the degradation of the co-component in a cellulose-polymer mixture. The presence of OR leads to an increase in thermal stability of HDPE, as was previously observed from the values of $T_{max}$ in TG/DTG curves. Therefore, cellulosic materials can be used as thermal stabilisers of polymers. This stabilisation caused by cellulosic materials can be attributed to an OR-HDPE interaction, either in the solid state or between HDPE and gases evolved from the OR degradation. The formation of char as a decomposition product of OR is the main factor to be taken into account in the changes in HDPE degradation processes. This behaviour was also noted for blends of biomass derivatives with other common polymers, such as polystyrene and polypropylene, with changes in the mechanism of thermal degradation [11, 12].

## Conclusions

A thermogravimetric study revealed that three stages of mass loss are involved during OR:HDPE decomposition. The first step, obtained in the temperature range (431–607 K), is attributed to the decomposition of hemicellulose. The second step occurs between 535 and 680 K, which corresponds to the decomposition of cellulose. The third step between 652 and 832 K was attributed to the decomposition of HDPE and lignin in the mixture.

The difference of mass loss ($\Delta m$) between experimental and theoretical, calculated as algebraic sums of the mixture for different heating rates of 2, 10, 20 and 50 K min$^{-1}$, is about 7–11% at 740–900 K. These experimental results indicate a significant synergistic effect during pyrolysis of OR mixed with HDPE.

For OR:HDPE mixture, in the three stages of the pyrolysis process, activation energies 155 kJ mol$^{-1}$ for the first stage, 212 kJ mol$^{-1}$ for the second one, and 220 kJ mol$^{-1}$ for the third one. When comparing with the pure materials, it is easy to note that the presence of HDPE does not significantly change the apparent activation energy of thermal decomposition of OR (with in the error of the method), but the $E$ value for HDPE in the mixture was somewhat lower than for the pure material. This effect is explained by the influence of the char on the radical degradation mechanism of the HDPE.

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