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ORIGINAL PAPER

Comparative pyrolysis of polyolefins (PP and LDPE) and PET

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Abstract In the present study, thermal degradation of polyolefins (PP and LDPE) and PET in a tubular reactor in an inert atmosphere was conducted. Each polymer was subjected to pyrolysis at the temperatures of 673, 773, 873, and 973 K. Yields of tar, residual coke and gas, and conversion degrees were calculated. Tars which include valuable chemicals were characterized by GC–MS, ^{1}H-NMR, FTIR, and GPC. Pyrolysis gases (C1 + C2, C3, C4, C5, and C6 + C7) were also analyzed by GC analysis. From the comparison of data, it can be said that pyrolysis of PP and LDPE leads to the formation of tar containing mainly paraffinic structures, while aromatic structures were produced by the pyrolysis of PET.

Keywords Polymer degradation · Pyrolysis · Polyolefins · Characterization

Introduction

In the latter years, the use of polyolefinic polymers has been growing up in a wide range of fields of applicability [1]. Principally, utilizations on fields of packaging, household accessories, toys, medical articles, and garden furniture are common. The increased using up of plastics in a modern community is unavoidable due to their versatile utilities, functional values, and the relatively small amount of energy required for their production, compared with other materials [2]. They replace materials such as metal, wood, paper, ceramics, and glass in a wide variety of uses. There are also new roles which only plastics can fulfil [3]. However, the getting rid

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of waste plastics is an important environmental problem in developed countries [4]. Since they are not easily bio-degradated and because of their weight-to-volume ratios, plastics are not suitable candidates for landfill [5]. Environmental defense requires increased recycling and reutilization in place of being landfilled or incinerated. Landfilling or incineration of plastic waste are not the right solutions because the former has the danger of leaching and soil impregnation of its degradation products and the end produce several pollutants that are perilous to the environment [6]. High damage of pollution control for incinerators and the decreasing acceptance of this method in waste management demand for alternative treatment of plastic wastes [7]. Similar to solid waste management, plastic waste recycling can also be categorized into four modes. Primary recycling deals with conversion into products of a nature similar to the original product. Secondary recycling (mechanical recycling) involves conversion into products of different forms for less demanding applications which can only be applied to thermoplastic materials. Tertiary recycling converts wastes into basic chemicals or fuels and is unique to plastics. Quaternary recycling retrieves energy from wastes through combustion.

Tertiary recycling such as thermolysis of plastic waste may have an important role in dealing with the immense amounts of plastic waste produced all over the world, by decreasing their deprecating effect on the environment. Plastic waste to feedstock of natural organic materials thermal processes can be a perspective for their conversion into valuable products [8]. This waste may be converted into economically valuable hydrocarbons, which can be used both as fuels and as feed stock in the petrochemical industry. One of the alternative ways for obtaining these products is the pyrolysis. Pyrolysis of plastic waste is proposed as a thermochemical recycling path, where the plastic waste materials are treated in an inert atmosphere [9]. By pyrolysis, used polymer materials can be converted into low molecular weight chemicals which can be used as raw materials for the chemical industry [10]. Alternatively, the oil may act as a feedstock for the steam cracker in the production of monomers to make new plastics. During this process, the polymeric structure is broken down to produce oil, gas, and char.

Numerous researchers have contributed to the theory and practice of thermal degradation (with or without catalyst) of polymers. Mainly polyolefins, polyethylene (PE), and polypropylene (PP) are the target polymers because their breaking down resulted in products with desirable properties for further application [11]. Pinto et al. [6, 12] investigated the effect of plastic mixture on product yield and composition. They detected end product yields and properties depend on the plastic waste composition. The presence of PE increases alkane content, while polyethylene terephthalate (PET) leads to higher aromatic content in the end product. The alkene formation benefited from the presence of PP [6].

Pyrolysis processes are generally classified into low, medium, and high temperatures based on the range of temperatures used to destroy the plastic structure [13, 14]. The corresponding temperatures defining the pyrolysis states are with the following temperature ranges <600 °C, 600–800 °C, and >800 °C [13, 15]. Low temperature processes generally enhance liquid products and high temperature processes enhance gaseous products [13].

The plastic polymer is thermally degraded, producing smaller intermediate species, which can further react and produce a mixture of smaller hydrocarbon molecules, liquids, and gases [6]. Both gaseous and liquid products are complex mixtures of hydrocarbons and other organic compounds, whose composition depends on the plastic waste composition [12].

In this work, the effect of temperature on product yield and composition structure of pyrolysis products was studied. Experiments were conducted at the temperatures of 673, 773, 873, and 973 K. The three main polymers which constitute the majority of plastics occurring in European municipal solid waste comprising PP (PP), Low Density Polyethylene (LDPE), and PET were pyrolyzed under the same operating conditions. The products of the thermal cracking were analyzed by using various spectroscopic techniques. Characterization of such pyrolysis liquids was performed by Gas Chromatography–Mass Spectroscopy (GC–MS), Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR), Fourier Transform Infrared Spectroscopy (FTIR), and Gel Permeation Chromatography (GPC). Analysis of the gaseous products was also performed by GC equipped with TCD detector.

Experimental section

Materials

The polymers (LDPE, PP, and PET) used in this research were in powder form which did not contain any stabilizers, fillers, and pigments. They were obtained from Özuğur-Akçim Plastic Company (Izmir, Turkey).

Pyrolysis procedure

Pyrolysis was conducted at the system given in Fig. 1. Each polymer was subjected to pyrolysis at the temperatures of 673, 773, 873, and 973 K. All experiments were carried out by a quartz reactor.

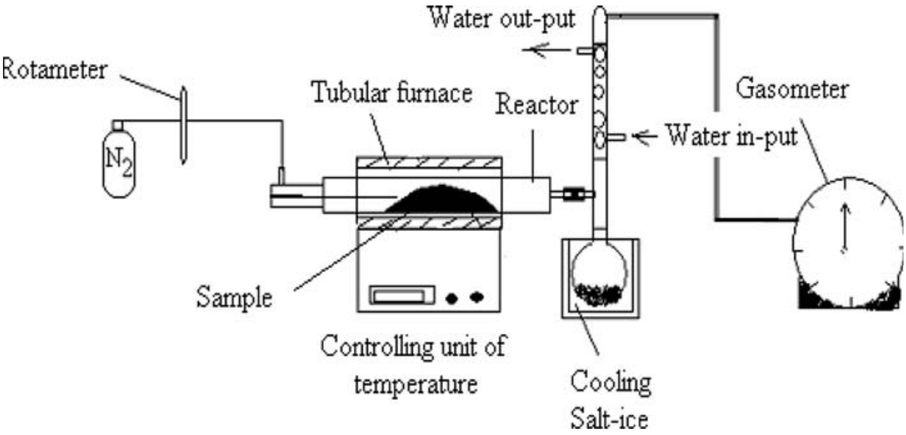


Fig. 1 Experimental setup for pyrolysis

The sample was loaded into the reactor which was inserted into the electrically heated fixed-bed furnace. The reactor was swept by nitrogen before heat through the tubular furnace. The rate of nitrogen flow through reactor and system apparatus was kept at 30 mL min^{-1}. Reactor was heated from room temperature to a determined temperature depending on reaction temperature, at a heating rate of 10 °C min^{-1}, and held at this temperature until no further liquid was produced. The internal reactor temperature was monitored by a thermocouple and controlled by variac. A thermocouple was inserted into the middle of the sample bed and the reactor tube was fitted into the stainless steel reactor. The outlet of the reactor was connected to a round-bottomed flask with a reflux condenser where condensation of pyrolysis occurred. The reaction mixture was cooled to about 0 °C with an ice-salt bath. The reaction products were classified into three groups: gases, liquid hydrocarbons (tar), and residual coke. The yield of tar is defined as the amount of liquid collected in the round-bottomed flask, and the yield of residual coke as the char remaining inside the reactor after the experiment. A gas meter connected to the end of the reflux condenser was used to measure the total volume of gas.

Characterization of the pyrolysis products

The pyrolysis products were also identified with various spectroscopic techniques. The paraffinic, olefinic, and aromatic hydrocarbons of the liquid products (tars) were analyzed [16]. GC–MS analysis of the tars was conducted by an AGILENT 6890 GC System 5973 MSD. GC–MS conditions were as follows: (column) HP1 (50 m × 0.32 mm × 0.52 μm); (carrier gas) He; (flow rate of He) 0.7 mL min^{-1}; (temperature program of oven) initial hold at 50 °C for 15 min, ramp to 300 °C at 5 °C min^{-1}, and hold for 17 min. The compounds found in tar were identified by comparison of their spectra with that in the NIST library of the GC–MS system as their peak area (%) in the total chromatogram.

The gas products were collected to a Tedlar bag. Its composition was determined with gas chromatography equipped with TCD detector (Agilent 6890) with an FID detector and a capillary GC alumina column (50 m _ 0.55 mm i.d.).

IR spectra of the tars as potassium bromide (KBr) discs of the samples were obtained by a MATTSON 1000 Model FTIR spectrophotometer.

^{1}H-NMR spectra of the tars were recorded by Bruker Avance DPX-400. ^{1}H-NMR was performed to estimate the hydrocarbon types and to provide an indication of product quality. From the ^{1}H-NMR spectra, the hydrocarbon types including aromatics, paraffins, and olefins were estimated using literature correlations developed by Myers et al. [16]. Spectral H-NMR regions were given in Table 1.

$$\text{Aromatics, vol.\%} = \frac{(A + C/3)0.97 \times 10^2}{(A + C/3)0.97 + (D - 2B + E/2 + F/3)1.02 + 3.33B}$$

$$\text{Paraffins, vol.\%} = \frac{(D - 2B + E/2 + F/3)1.02 \times 10^2}{(A + C/3)0.97 + (D - 2B + E/2 + F/3)1.02 + 3.33B}$$

Table 1 Spectral H-NMR regions

	Type of proton	Chemical shift region (ppm)
A	Ring aromatics	6.6–8.0
B	Olefin	4.5–6.0
C	α-Methyl	2.0–3.0
D	Methine (paraffins)	1.5–2.0
E	Methylene (paraffins)	1.0–1.5
F	Methyl (paraffins)	0.6–1.0

$$\text{Olefins, vol.\%} = \frac{3.33B \times 10^2}{(A + C/3)0.97 + (D - 2B + E/2 + F/3)1.02 + 3.33B}$$

$$H/C = \frac{A + B + C + D + E + F}{(A + C/3)1.28 + (D - 2B + E/2 + F/3)1.02 + 3.42B}$$

The molecular weight distributions of the tars were measured by Agilent 1100 GPC/SEC/RID instruments using Zorbax columns (PSM 60 5 × 10^2–10^4). The samples were dissolved in tetrahydrofurane (THF). The temperature of the column oven was 30 °C, and a volume rate of 1 mL min^{-1} of each sample was injected. THF was used as eluent with a flow rate of 1 mL min^{-1}. A refractive index detector (RID) was used as the detector. GPC is also called size exclusion chromatography affords a rapid method for the separation of oligomeric and polymeric species. The separation is based on the differences in molecular size in solution. It has had widespread applications. GPC is appropriate for both polar and non-polar analytes, therefore, it can be effectively used to cleanup extracts containing a broad range of analytes. It is of particular importance for elimination from the sample of lipids, proteins, viruses, steroids in biological systems and is the method of choice for determining molecular weight distribution of synthetic polymers. For determining the molecular weight of synthetic polymers, at least 50 types of polymers have been characterized.

The molecular weight distribution of the tars was determined as number (M_n) and weight average (M_w), in addition viscosity average molar mass (M_v) and the polydispersity index (D) of the tars were calculated. The number average molecular weight (M_n) is defined as the average molecular weight according to the number of molecules present of each species. The weight average molecular weight (M_w) is the sum of the product of the weight of each species present and its molecular weight divided by the sum of the weights of the species [17].

Thermogravimetric (TG) analysis of polymers (LDPE, PP, and PET) was carried out using a Shimadzu TG-60H instrument. The polymer samples were placed in a platinum pan and the experiments were done under nitrogen atmosphere with a flow rate of 30 mL min^{-1}. The temperature was increased from room temperature to 1,000 K at 10 °C min^{-1} of heating rate.

Results and discussion

TG results

The TG curves for the degradation of PP, LDPE, and PET are shown in Fig. 2. Degradation temperatures of polymers are between the temperatures 700 K and 775 K. For PET, the maximum weight loss of 60% occurs at 715 K due to thermal degradation of the PET backbone. The maximum weight loss of PP and LDPE shifted to higher temperature region, respectively. In addition, thermal stability of LDPE is higher than PP and PET.

Product distributions

The effects of pyrolysis temperatures (673, 773, 873, and 973 K) on the tar and gas yields and on conversion degrees are shown in Figs. 3, 4, 5, respectively. The tar yields obtained at 673 K are lower than that obtained at other temperatures. A properly decrease in tar yields obtained by pyrolysis of PET is seen. Apparently, it is possible to obtain more tar at lower temperatures during the pyrolysis of PET. 873 K is expected to be the most suitable temperature for maximum tar yield in the presence of LDPE. The maximum tar evolution for PP and PET occurred at 773 K.

It can be said that gas yields were higher at the temperatures, in which the tar yields were lower. According to the literature, gaseous products of degradation of polyolefinic polymers consist mainly of low molecular weight volatile hydrocarbons such as C1–C4 (methane, ethane, propane, and butane) [18–20]. In PET pyrolysis, gaseous products increase with increasing temperature. During PET pyrolysis CO, CO_2 were formed mainly by the decomposition of containing oxygen components. It was explained by decarboxylation of end groups to CO, CO_2 as the temperature

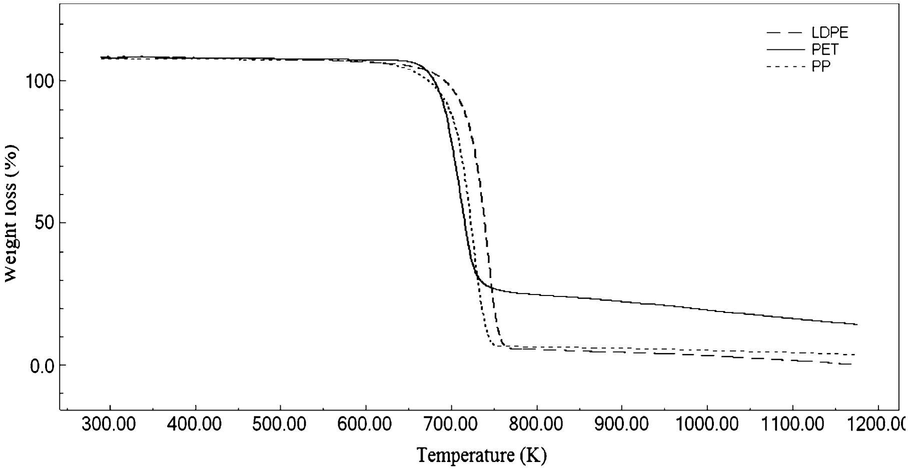


Fig. 2 TG curves of the polymers

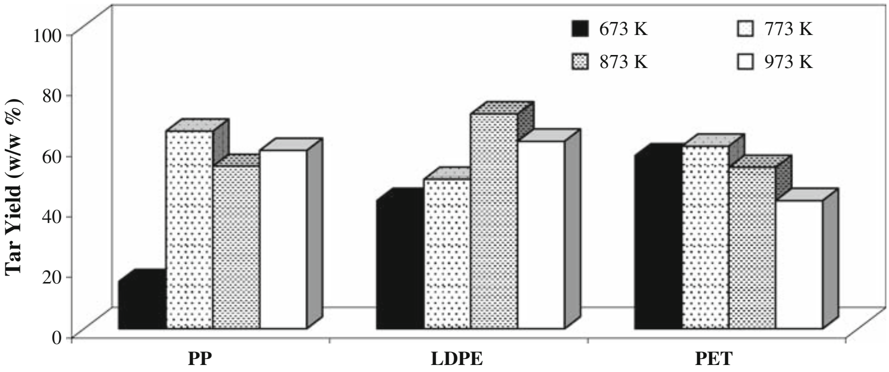


Fig. 3 Tar yields from the pyrolysis of PP, LDPE, and PET at different temperatures

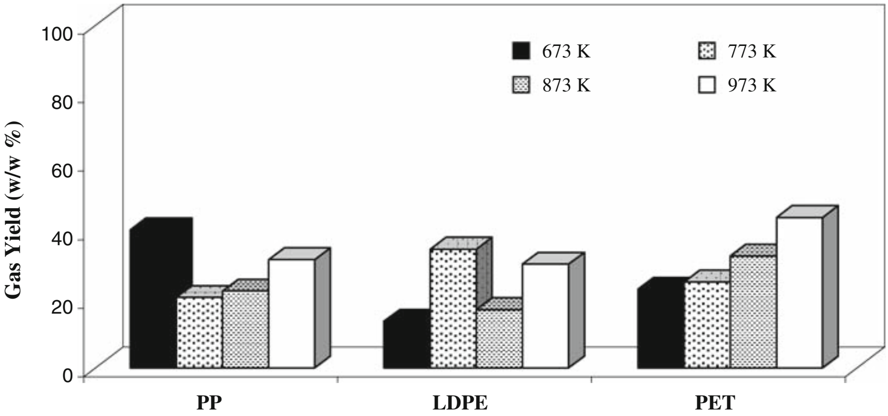


Fig. 4 Gas yields from the pyrolysis of PP, LDPE, and PET at different temperatures

rises [19]. In general, tar yields were higher than gas yields and this shows that conversion of polyolefins to tar mainly occurred.

The main task of thermal cracking is decomposition of large (long) hydrocarbon molecules into smaller ones. High-molecular feedstock, such as plastic chains scission, so lower molecular paraffins and α-olefins occur [21].

$$\mathrm{R{-}CH_2{-}(CH_2)_{\mathit{x}}{-}CH_2{-}CH_3 \rightarrow R{-}(CH_2)_{\mathit{m}}{-}CH_3 + CH_3{-}(CH_2)_{\mathit{n}}{-}CH = CH_2}$$

Cracking of primary products, olefins, give higher molecular hydrocarbons by polymerization or tar and coke.

$$\mathrm{CH_2 = CH_2 + CH_3{-}CH = CH_2 \rightarrow CH_3{-}CH_2{-}CH_2{-}CH = CH_2}$$

$$\mathrm{R{-}CH_2{-}CH = CH_2 + R{-}CH_2{-}CH = CH_2 \rightarrow tar,\ coke}$$

A reversible free radical mechanism plays an important role on the formation of tar and coke [22, 23]. These reactions provide opportunities for both making and

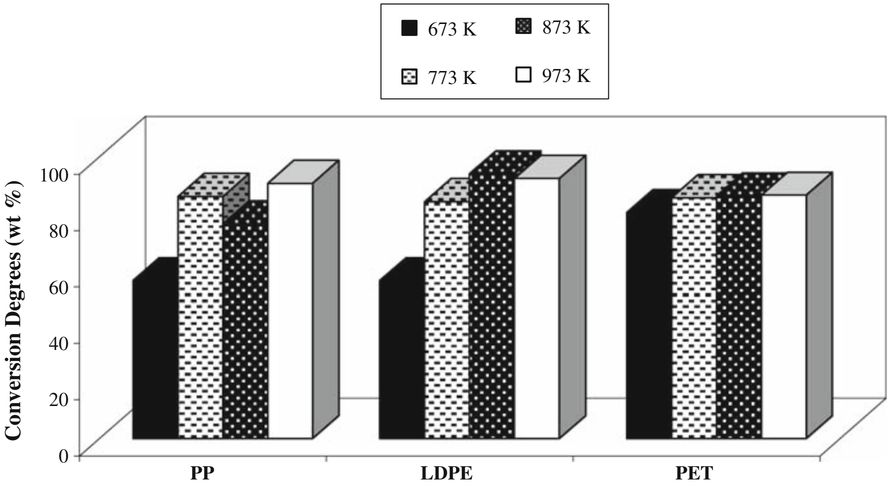


Fig. 5 Conversion degrees for the pyrolysis of PP, LDPE, and PET at different temperatures

breaking chemical bonds and consequently, thermal hydrocarbon chemistry can involve the degradation of large molecules into smaller ones, but it can also involve molecular growth and the production of heavier molecules [22].

$$\mathrm{R{-}CH_2{-}CH_2{-}CH_2{-}CH_3 + CH_3^{\bullet} \rightarrow R{-}CH_2{-}CH_2{-}CH_2{-}CH_2^{\bullet} + CH_4}$$

Free radicals react with hydrocarbons and produce new hydrocarbons and new free radicals.

$$\mathrm{R1{-}CH_2{-}CH_2{-}CH_2{-}R2 + R3 \rightarrow R1{-}CH_2{-}CH^{\bullet}{-}CH_2{-}R2 + R3H}$$

$$\mathrm{R1{-}CH_2{-}CH^{\bullet}{-}CH_2{-}R2 + R3 \rightarrow R1{-}CH_2{-}CH{-}CH_2 + R2^{\bullet}}$$

Cracking of PP, LDPE, and other polyolefins occurs by random chain scission and therefore a broad hydrocarbon spectrum is produced. At higher cracking temperature other reactions, i.e., cyclization and dehydrogenation of naphthenes and hydrocarbon pyrolysis with production of benzene and ethylene, butadiene and hydrogen are also possible.

The reason for the char formation can be thought to be the poor mobility of the thermally generated free radicals at low temperature. Another reason might be the poor carbon–carbon bond scission in the chain at this temperature. Carbon–carbon bond scission needs energy >68 kJ mole^{-1}. To have efficient C–C bond cleavage, the temperature must be sufficiently high [24].

Lower yields of tars obtained by PP and LDPE pyrolysis at 673 K revealed that the decomposition initiates at very low temperatures, but 673 K is not high enough temperature for the conversion of polymers to tars. Degradation of polyolefinic polymers proceeds via a radicalic mechanism, leading to the formation of free radicals. These radicals are formed by scission of weak bonds, having energy lower than 58 kcal mol^{-1} [25]. The radicals generated as a result of the scissions due to thermal shock need to be stabilized, otherwise reunion of the radicals occurs, leading to char formation. In addition, the rate of the free radicals generated is low at lower temperatures and char formation is enhanced since the required energy for scission of C–C bonds (>68 kJ mol^{-1}) cannot be supplied by the radicals. An increase in temperature leads to an enhancement in the bond scission. Thus, the saturation of radicals is occurred by the help of hydrogen generated, leading an increase in tar yields. Secondary polymerization reactions occurred at higher temperatures leads to the improved char yields, while tar yields are decreased in this case. Gas yields are improved even in higher temperatures.

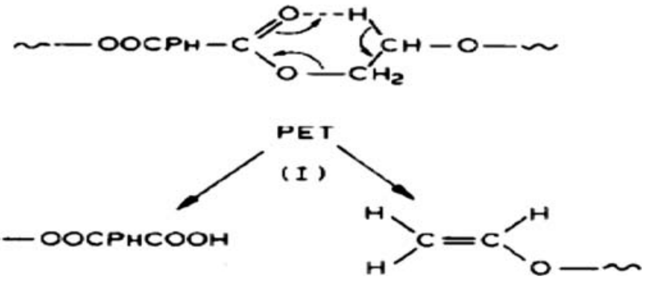
$$n\text{-Paraffins} \rightarrow \text{Olefins} \rightarrow \text{Naphthenes} \rightarrow \text{Aromatics}$$

The maximum tar yield obtained for the PP pyrolysis is obtained at 773 K (Fig. 3). Increases in temperature further, tar yields were partly decreased. On the other hand, the char yield obtained by LDPE pyrolysis was decreased at 873 K, while tar yields were improved in this temperature.

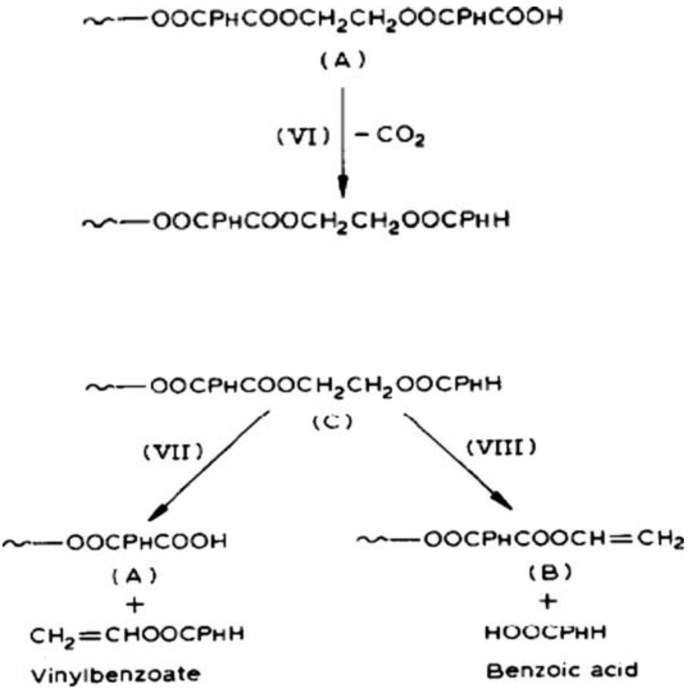
PET, which contains oxygen and aromatic containing groups degraded generally via decarboxylation. Combining radicals lead to the formation of higher molecular weight products and gas products (CO and CO_2). The primary degradation of PET structure might be attributed to a random scission of ester links in the main chain as given in Scheme 1 [25]. Carboxylic acid and olefinic end groups form in the first step because of the ester scission reaction.

Subsequently, rapid production of low molecular weight volatile fragments was occurred [25]. This volatiles were mostly COOH, acetaldehyde, CO, CO_2, C_2H_4, H_2O, and CH_4 [26]. The carboxylic acid end group products can undergo decarboxylation to yield phenyl end group compounds as shown in Scheme 2. Subsequently, benzoic acid and vinyl benzoate are formed by scission of phenyl end group compounds.

Therefore, decarboxylation and disintegration continue during pyrolysis, the other volatile products formed from vinyl benzoate and benzoic acids were benzene, toluene, styrene, and ethyl benzene. The formation of these compounds can be explained through the secondary reactions which were taking place on the primary degradation products. This shows that the volatile product formation was increased at higher temperatures for the pyrolysis of PET.



Scheme 1 The reaction pathway for the primary degradation of PET



Scheme 2 The reaction pathway for the secondary degradation of PET

Analysis of the gaseous products

Figure 6 shows the weight fraction of the gaseous products obtained during the pyrolysis of polymers at 973 K. The hydrocarbons with three carbon atoms are the most abundant gaseous species in the case of PP. Pyrolysis of PET leads to the formation of gaseous products consisting mainly of C1 + C2 hydrocarbons, while C4 and C6 + C7 were the main products for the pyrolysis of LDPE comparing with the other polymer types.

These observations show that C6 + C7 components degraded to the other lighter gaseous products detected as a result of the pyrolysis of PP and PET. Distribution of the gaseous species approximately the same in the pyrolysis of LDPE with the exception of C3 hydrocarbons.

Characterization of liquid products

GC–MS results

Composition of the tars for the thermal degradation of PP, LDPE, and PET at 973 K is summarized in Table 2 as the relative peak area. PP and LDPE decomposed into a large number of aliphatic compounds. The oil products of LDPE were found to be consist of mainly C8–C30 hydrocarbons. The aromatic content was observed only in

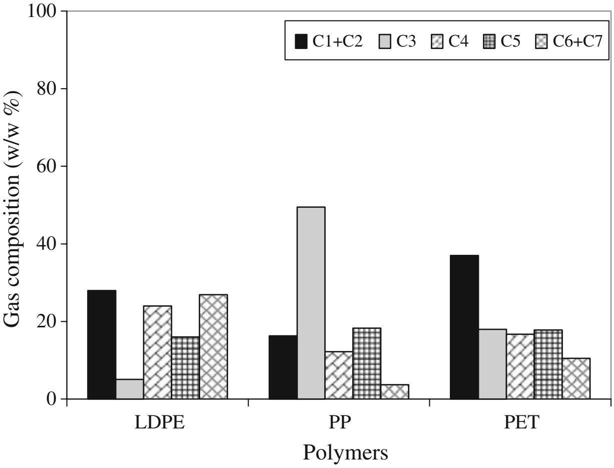


Fig. 6 Amount of gaseous products obtained from the pyrolysis of LDPE, PP, and PET at 973 K

the cracking products of PET. The composition of the alkene products as well as alkane products was very similar for pyrolysis of PET. Tar from PET pyrolysis consists of benzoic acid and derivative, biphenyl, anthracene, and terphenyl. The % area of aromatic hydrocarbons decreased slightly for PP and LDPE degradation compared to PET degradation. Kaminsky and co-workers also found similar results. The pyrolysis products PE and PP were mainly aliphatic alkanes and alkenes [15]. However, Vıjayakumar and Fink remarked that the products from PET pyrolysis had highly aromatic character [21].

In addition, the linear alkane structures formed more readily in LDPE pyrolysis compared to the PP pyrolysis. The cyclo structures were mainly from PP pyrolysis, while no cyclic structures are found during LDPE pyrolysis. Amounts of 2,4-diethyl-1-methyl-cyclohexane and 1,2-diethyl-3-methyl-cyclohexane were remarkable. Major compounds were C9 compounds, like 2-methyl-4-octene, 2-methyl-2-octene, 2,6-dimethyl-2,4-heptadiene, 2,4-dimethyl-1-heptene, 2-methyl-1-octene. As a result, the amount of unsaturated hydrocarbons (olefins) was high in the products. It is well known that the thermal degradation of polyolefinic polymers occurs by the random scissoring of the long polymeric chain and the products of degradation are distributed in a wide range of molecular weights. Therefore, the amount of total (% of area) unsaturation of liquid products for thermal degradation of PP is lower than that for thermal degradation of LDPE.

Thermal degradation mechanisms of the polyolefinic plastics leading to the formation of various reaction products has been investigated by a range of researchers. It is suggested that the thermal degradation of HDPE and LDPE occurs via random scission to yield a wide spectrum of hydrocarbon fragments which may contain any number of carbon atoms. The C–C bond is the weakest in the HDPE and LDPE structure. However, during the degradation process the stabilization of the resultant radical after chain scission leads to the formation of carbon double bonds, C=C, in the structure. The large number of compounds with carbon double bonds

Table 2 GC–MS compositions of tars obtained from the pyrolysis of LDPE, PP, and PET at 973 K

Name of compounds	% Area		
	LDPE	PP	PET
Alkanes			
Octadecane	1.74	0.26	0
Eicosane	4.86	1.88	0
Nonadecane	2.09	0	0
Heneicosane	1.6	0	0
Hexadecane	1.57	0	0
Docosane	1.56	0	0
Tetracosane	1.33	0	0
Decane	1.35	0	0
Dodecane	1.51	0	0
Heptadecane	1.59	0	0
Pentacosane	1.17	0	0
Pentadecane	1.79	0	0
Tetradecane	1.66	0	0
Tridecane	1.61	0	0
Undecane	1.46	0	0
Cyclotetracosane	2.06	0	0
(1.alpha, 3.alpha, 5.alpha)-1,3,5-trimethyl-cyclohexane	0	2.14	0
2,4-Diethyl-1-methyl-cyclohexane	0	15.78	0
1-Ethyl-2-propyl-cyclohexane	0	2.37	0
1,2,3-Trimethylcyclohexane (1r,2t,3c)	0	3.31	0
1-Ethyl-2,4-dimethyl-cyclohexane	0	2.01	0
1,2-Diethyl-3-methyl-cyclohexane	0	9.16	0
Trans-2-(1-methylethyl)1,1′-bicyclohexyl	0	2.57	0
1-Isopropyl-1,4,5-trimethylcyclohexane	0	2.71	0
Alkenes			
2,4-Dimethyl-1-heptene	0	3.95	0
4-Methyl-2-undecene	0	2.95	0
1-Hexacosene	0	1.60	0
1-Nonadecene	2.73	0	0
1,12-Tridecadiene	1.39	0	0
1,15-Hexadecadiene	1.67	0	0
1,19-Eicosadiene	4.19	0	0
1,21-Docosadiene	2.3	0	0
1-Decene	2.87	0	0
1-Docosene	1.46	0	0
1-Dodecene	2.61	0	0
1-Hexadecene	2.88	0	0
1-Nonene	2.73	0	0
1-Octadecene	3.36	0	0

Table 2 continued

Name of compounds	% Area		
	LDPE	PP	PET
1-Pentadecene	3.02	0	0
1-Tetradecene	2.96	0	0
1-Tridecene	2.63	0	0
2-5-Nonadecene	2.5	0	0
3-Heptadecene,(Z)-	3.11	0	0
Z-12-pentacosene	2.83	0	0
Undecene	2.84	0	0
Z-12-pentacosene	2.83	0	0
Z-5-nonadecene	8.15	0	0
Aromatics			
Naphthalene	0.99	0.756	1.063
2-Phenyl-Naphthalene	0	0	1.247
Biphenyl	0	0.177	17.127
Acetophenone	0	0	2.625
1-Phenyl-1,2-propanedione	0	0	1.777
4-Methyl-1,1′-biphenyl	0	0	1.483
3-(3-methoxyphenyl)-1H-1,2,4-triazole	0	0	2.268
1-(1,1′-biphenyl)-4-yl-ethanone	0	0	1.086
Triphenylene	0	0	1.149
m-Terphenyl	0	0	2.484
p-Terphenyl	0	0	2.904
3′-Methyl-1,1′:4′,1″-terphenyl	0	0	1.033
1,1′:3′,1″:4″,1‴-quaterphenyl	0	0	1.832
Anthracene	0	0	3.451
Styrene	1.07	0	0.478
2-Phenyl-5-bezylideneamino-benzimiazole	0	0	3.072
Dibenzoate-1,2-ethanediol	0	0	1.172
Benzoic acid	0	0	23.707
4-Methyl-benzoic acid	0	0	1.621
4-Ethylbenzoic acid	0	0	1.308
4-Acetylbenzoic acid	0	0	10.29
Total area	93.28	52.473	72.42

was shown by the higher concentration of alkenes in the resultant pyrolysis oil/wax. The thermal degradation of PP has also been assigned to a random scission reaction which leads to the formation of a large number of hydrocarbon species. As similar structure of PP with that of HDPE and LDPE, thermal degradation of these polymers also results in a series of alkanes, alkenes, and alkadienes.

Aromatic structures are mainly formed by PET degradation as revealed in GC–MS results. Free radical mechanism and decarboxylation play an important role in the product distribution of PET pyrolysis. Successive formation of a free carboxylic acid and an ethenyl ester-group-terminated macromolecular fragment leads finally to mono- and diethenyl terephthalate. Smaller aromatic fragments were formed at higher temperatures [26].

Benzoic acid has been identified as a major constituent in oils derived from the pyrolysis of PET while other aromatic compounds identified included phenyl and naphthalene and other polycyclic aromatic hydrocarbons. Benzoic acid and biphenyl contents of the tars obtained by PET pyrolysis attracted attention.

^{1}H-NMR results

The hydrocarbon types (aromatics, paraffins, and olefins) detected were given in Fig. 7. More paraffinic structures were found in the case of LDPE compared to PP, while no paraffinic structure was detected in the case of PET. Pyrolysis of PET leads mainly to the formation of aromatic constituents.

FTIR results

Figure 8 shows the FTIR spectra of the tars obtained from thermal degradation of PP, LDPE, and PET at 973 K. The spectra were very similar for the tar of polyolefins since their polymer structures were very similar and their thermal degradations were likely to produce similar compounds in the pyrolysis product, whereas there are clear differences between the tars of polyolefins and PET (Fig. 8). The main differences between PP and PET are observed on the characteristic bands of C–H structure. The region between 700 and 900 cm^{-1} contains various bands related to aromatic out of plane C–H bending in the tar obtained of PET. The intensity of this peak was weak in LDPE spectra. The analysis of the regions between 2,800–2,980 cm^{-1} and 1,480–1,370 cm^{-1} in the spectra of tars obtained by pyrolysis of polyolefins shows that aliphatic hydrogen was mainly as –CH$_2$ structures. The tars obtained from the pyrolysis of polyolefins contain a higher content of paraffinic groups than the tar of PET. In FTIR spectra of tar of PP, the intensity peak at 1,375 cm^{-1} shows of –CH$_3$ groups. This indicates that the most of

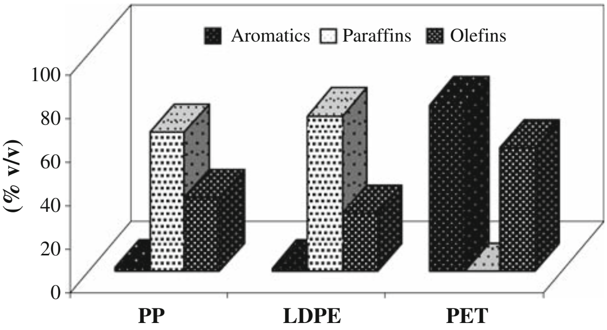


Fig. 7 The amounts of hydrocarbon types in the tars obtained from the pyrolysis of PP, LDPE, and PET at 973 K

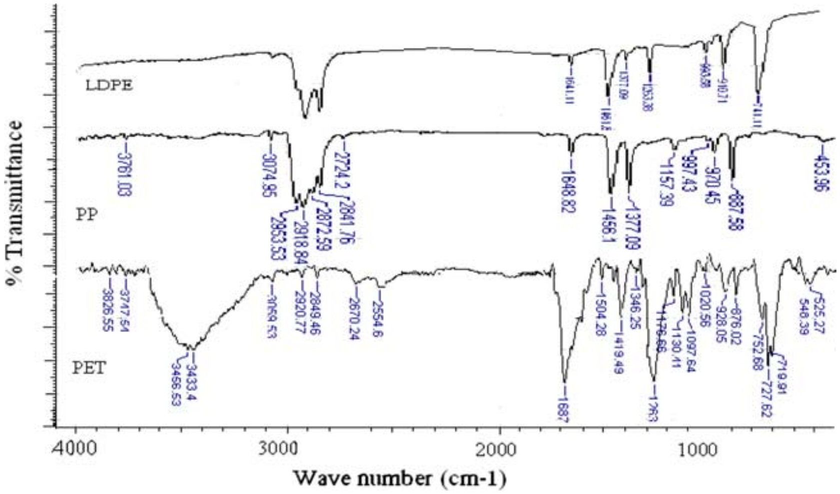


Fig. 8 FTIR spectrums of the tars obtained from the pyrolysis of PP, LDPE, and PET at 973 K

the aliphatic structures in the tar of PP exist as cyclic structures, whereas in the tar of LDPE the aliphatic chains predominate. The pyrolysis of PP and LDPE produced a strong presence of aliphatic functional groups. Aliphatic peaks in FTIR spectra's of PP and LDPE were mainly observed, while the intensity of aromatic bonds in spectra was weak, which were also found by GC–MS and ^{1}H-NMR.

The presence of C–C stretching vibrations between the wavelengths 1,765 and 1,625 cm^{-1} suggests the presence of alkenes. The intensity of this peak was quite remarkable in PET spectra, while the intensity of the peak was decreased in PP spectra. In LDPE spectra, there was no peak representing C–C stretching vibrations. This observation is also supported by ^{1}H-NMR analysis. The bands at the nearby 3,200–3,600 cm^{-1} represent –OH stretching vibrations indicating the presence of phenols and alcohols found in the tar obtained by PET pyrolysis. The band in 1,260–1,280 cm^{-1} indicates C–O–C etheric structure.

GPC results

The tars obtained from pyrolysis of PP, LDPE, and PET were analyzed by GPC to determine the molecular weight distribution of the tars. Table 3 shows the mass average (M_w), the number average (M_n), and the viscosity average (M_v) of the tars obtained from pyrolysis of LDPE, PP, and PET at 973 K. Tar obtained by pyrolysis of PET has the lowest M_w (226), M_n (175), and M_v (226). M_w, M_n, and M_v values of tars obtained by PP and LDPE pyrolysis were close to the each other and higher than that obtained by pyrolysis of PET. The increased tar yield leads to an increase in the number of higher molecules in the case of tars from PP and LDPE, while degradation of PET to gases is the reason for smaller molecular fragments.

Table 3 Molecular weight distributions of the tars obtained from the pyrolysis of PP, LDPE, and PET at 973 K

	PP	LDPE	PET
Molecular weight numbers			
$\overline{M}_{\mathrm{w}}$ (g/mol)	280	277	226
$\overline{M}_{\mathrm{n}}$ (g/mol)	181	182	175
$D = \overline{M}_{\mathrm{w}}/\overline{M}_{\mathrm{n}}$	1.55	1.52	1.29
$\overline{M}_{\mathrm{v}}$ (g/mol)	280	278	226

M_{v} was related to the density of molecules found in tar. Thus, it can be concluded that the low viscosity of tar from PET pyrolysis represents that this tar contains the low molecular weight molecules.

Table 3 shows also the ratio of M_{w} and M_{n} representing dispersity (D), which is a measure of the homogeneity of the fragments. Furthermore, the polydispersity reflects the deviation of the molecular weight distribution from distribution of an ideal single compound. Single compounds have a polydispersity in the range 1.0–1.1. Polydispersity values of the tars obtained by PP and LDPE pyrolysis were close to each other, since the M_{w} values of tars from PP and LDPE pyrolysis are close to each other. Polydispersity of the tar from PET pyrolysis are lower than the other two tars and close to 1.0. A higher polydispersity for a sample indicates a broader range of molecular weight distribution, reflecting a wider range of compounds present in the sample. Actually, formation of long chain alkanes and cyclo structures plays an important role in increasing average molecular mass and polydispersivity. On the other hand, degradation of PET to short chain aromatic structures leads to a decrease in average molecular mass and polydispersivity.

Figure 9 represents that LDPE and PP show a similar and very wide molecular weight distribution, whereas PET gave peak in the lower molecular weight region and narrow molecular weight distribution since M_{n} and M_{w} values are close to each other.

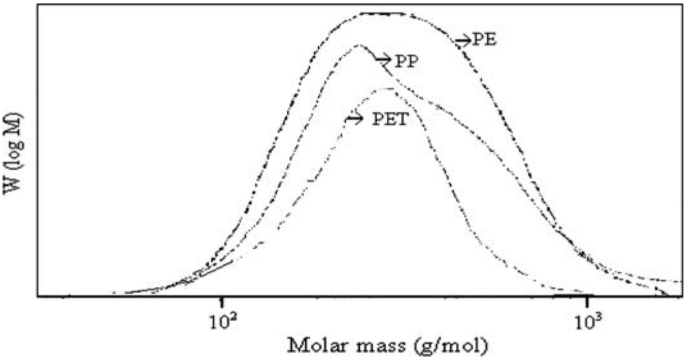


Fig. 9 Molecular weight distributions of tars obtained from the pyrolysis of PP, LDPE, and PET at 973 K

Conclusions

Degradation of polyolefinic polymers proceeds via a radicalic mechanism, leading to the formation of free radicals. These radicals are responsible for the formation of low molecular weight gases. PP has more tertiary carbon atoms and therefore is more reactive than LDPE. As a result of this, more gas is generated at low temperatures in the presence of PP. Pyrolysis of PP and LDPE produces tar containing paraffinic and olefinic structures, while PET pyrolysis leads to the formation of tar, which has mostly aromatic structure. C3 hydrocarbons were significantly evolved by pyrolysis of PP, while C1 + C2 are the main hydrocarbon types generated in the case of PET pyrolysis. Pyrolysis of LDPE leads to the formation of C1 + C2, C4, and C6 + C7 mainly.

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