

# Recycling of PET Post-consumer Bottles: Effect of the Re-extrusion Process on the Structure, Thermal Properties, and Apparent Activation Energy

M. Jakić,\* S. Perinović Jozić, I. Bandić, and L. Ključe

This work is licensed under a Creative Commons Attribution 4.0 International License



University of Split, Faculty of Chemistry and Technology, Ruđera Boškovića 35, 21 000 Split, Croatia

## Abstract

In this work, post-consumer poly(ethylene terephthalate) (PET) bottles were gathered, separated from other materials, and re-extruded. In order to evaluate the effect of re-extrusion on the structure of PET, Fourier transform infrared spectroscopy was utilised. No significant effect of the re-extrusion process on the structure of the PET sample was noticed. Obtained samples were also characterised by differential scanning calorimetry (DSC) in order to determine characteristic thermal transitions of PET. DSC results indicated the influence of re-extrusion; extruded PET started to melt at lower temperatures, and the crystallisation of re-extruded PET took place at significantly higher temperatures in comparison to PET. Likewise, thermogravimetric analysis (TG) was used to evaluate the effect of re-extrusion process on the thermal stability of samples. TG analysis revealed that the re-extrusion process had no effect on the thermal stability of the investigated PET samples. Finally, the activation energy of thermal degradation of the investigated samples was calculated using iso-conversional Flynn-Wall-Ozawa and Friedman method. Consequently, higher activation energies were noticed for the re-extruded PET sample in comparison to the PET bottle sample, which is a good argument in support of PET bottle recycling.

## Keywords

Poly(ethylene terephthalate), post-consumer bottles, recycling, re-extrusion, thermal properties, activation energy

## 1 Introduction

Poly(ethylene terephthalate) (PET) is a thermoplastic polyester mainly used for packaging and textile production. Hence, it is one of the main polymer materials, which can be found in municipal waste. Thanks to its durability, strength, and transparency, PET is widely used in the production of disposable carbonated beverage or milk bottles. Since PET packaging has a short useful life and large production volume, new issues in determining the most appropriate final destination have emerged.<sup>1</sup> The problem of post-consumer PET bottles could be dealt with in quite different ways. Although the cheapest, landfilling is environmentally and economically the worst possible option. Fortunately, there are many better solutions, like chemical recycling, mechanical recycling, and incineration.<sup>1</sup> In order to choose the proper solution, many countries have utilised life cycle assessment (LCA) as a common technique to evaluate the environmental impact of PET packaging. In that sense, Japan and China have compared the mechanical recycling, chemical recycling, incineration, and landfilling of PET post-consumer bottles.<sup>2</sup> The conclusion was quite unambiguous; mechanical recycling exhibited less global warming potential (GWP) and fossil resource consumption than the other options. As expected, landfilling had the highest fossil resource consumption. Thanks to the packaging waste management fee,<sup>3</sup> the post-consumer PET bottle is the most recycled polymer material in Croatia. In

that way, a large quantity of sorted and relatively clean material could become available for the traditional low-value mechanical recycling via melting and re-extrusion. However, current mechanical recycling processes are limited by their cost, degradation of mechanical properties, and inconsistent quality of products.<sup>4</sup>

Since the extrusion process is considered to be cheap, large-scale, solvent-free, and applicable to many polymers, it is the most utilised method in mechanical recycling industries to produce re-granulated material from common waste plastics.<sup>5</sup> However, during extrusion, thermo-oxidative and shear-induced chain scission, chain branching or crosslinking of the polymer material may occur,<sup>4</sup> worsening its mechanical properties and processability.<sup>6</sup> Degradation can be partially controlled by varying the extrusion temperature and screw speed. Re-extruding at excessive temperatures and screw speeds could accelerate chain scission, thus resulting in unprocessable polymer material.<sup>6</sup> An additional problem during PET recycling process are other materials, like paper and poly(vinyl chloride) (PVC) (labels), and polyethylene (PE) or polypropylene (PP) (cap). If not removed during preparation stage, these materials could alter properties of the recycled PET.<sup>7</sup> Likewise, after sorting and prior to extrusion, PET needs to be washed at elevated temperature in alkali solution and rinsed in water in order to remove impurities (content from bottle) and adhesive (label). Finally, to prevent possible hydrolytic degradation of PET (polyester) during recycling, the moisture needs to be removed (drying at elevated temperatures).<sup>8</sup>

Hence, in this work, post-consumer PET bottles were gathered and separated from other materials in order to obtain

\* Corresponding author: Assist. Prof. Miće Jakić  
Email: [mice.jakic@ktf-split.hr](mailto:mice.jakic@ktf-split.hr)

only PET material. The obtained PET bottles were then shredded into smaller pieces and re-extruded. In this regard, the goal of this research was twofold: (1) to evaluate the effect of re-extrusion process on the thermal properties of PET, and (2) to calculate the activation energy of the thermal degradation of recycled PET experimentally determined by TG analysis.

## 2 Experimental

### 2.1 Materials and preparation

The post-consumer bottles made from transparent PET were gathered at the Faculty of Chemistry and Technology from colleagues and students. Caps and labels were removed, leaving only the PET polymer material (bottle). Bottles were then thoroughly washed and dried for 24 h at 120 °C, after which they were shredded into smaller pieces. These small pieces were marked as PET samples. Recycling was carried via re-extrusion in a laboratory single-screw extruder (Dynisco, Qualitest North America) at 235 °C and at screw speed of 100 rpm. The extruded filaments were marked as e-PET samples. The re-extrusion temperature was selected according to the melting transition and onset temperature of thermal degradation of the neat PET, respectively.

### 2.2 Methods of characterisation

#### 2.2.1 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) spectra of the PET and e-PET samples were recorded on a Perkin Elmer Spectrum Two FT-IR spectrometer by the universal attenuated total reflectance (UATR) technique with diamond reflection crystal. The spectra were collected in 10 scans at a resolution of 4 cm<sup>-1</sup> and in the range of 4000–450 cm<sup>-1</sup> at room temperature.

#### 2.2.2 Differential scanning calorimetry

Thermal properties of PET and e-PET samples were investigated by Mettler Toledo DSC 823e calorimeter in nitrogen atmosphere (30 cm<sup>3</sup> min<sup>-1</sup>). Samples of approximately 15 mg were heated at a rate of 20 °C min<sup>-1</sup> from 25 to 300 °C, cooled at the same rate to 25 °C, and reheated to 300 °C. The glass transition temperature ( $T_g$ ) was determined from the second heating cycle as the extrapolated onset temperature ( $T_{eig}$ ), as midpoint temperature ( $T_{mg}$ ), and extrapolated end temperature ( $T_{efg}$ ); the corresponding change of the specific heat capacity ( $\Delta C_p$ ) was determined as well, all according to international standard ISO 11357-2.<sup>9</sup> The melting point, crystallisation temperatures, and corresponding enthalpy of melting and crystallisation ( $\Delta H_m$  and  $\Delta H_c$ ) were determined according to international standard ISO 11357-3.<sup>10</sup> The melting/crystallisation temperatures ( $T_m/T_c$ ) were determined as the extrapolated onset temperature ( $T_{eim/c}$ ), peak temperature ( $T_{pm/c}$ ), and extrapolated end temperature ( $T_{efm/c}$ ). The degree of crystallinity was calculated according to Eq. (1):

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \cdot 100 \quad (1)$$

where  $\Delta H_m$  and  $\Delta H_m^0$  are apparent melting enthalpies per gram of post-consumer PET bottle material and of 100 % crystalline PET (140 J g<sup>-1</sup>),<sup>11</sup> respectively.

#### 2.2.3 Thermogravimetric analysis

Thermogravimetric measurements were performed by a PerkinElmer Pyris 1 TGA thermobalance at three different heating rates (2.5, 5, and 10 °C min<sup>-1</sup>) in the temperature range 50–650 °C in nitrogen (20 cm<sup>3</sup> min<sup>-1</sup>). The sample mass was approximately 10 mg. From thermogravimetric curves (TG) and corresponding derivative thermogravimetric curves (DTG), the following characteristics were determined: onset temperature ( $T_{onset}$ ), temperature at 5 % mass loss ( $T_{5\%}$ ), temperature at the maximum degradation rate ( $T_{max}$ ), maximum degradation rate ( $R_{max}$ ), final mass ( $m_f$ ), and mass loss ( $\Delta_m$ ) for the observed degradation steps.

## 3 Nonisothermal degradation kinetics analysis

To predict the thermal behaviour of recycled PET after re-extrusion process and to give TG data proper meaning, kinetic analysis is the most convenient tool. Kinetic analysis of the solid-state reactions that are ruled by a single process is based on the Eq. (2):

$$\frac{d\alpha}{dt} \cong \beta \frac{d\alpha}{dT} = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot f(\alpha) \quad (2)$$

where  $\alpha$  is the degree of conversion,  $\beta$  is the linear heating rate (°C min<sup>-1</sup>),  $T$  is the absolute temperature (K),  $R$  is the general gas constant (J mol<sup>-1</sup> K<sup>-1</sup>),  $t$  is the time (min),  $A$  is the pre-exponential factor,  $E$  is the activation energy, and  $f(\alpha)$  is a reaction model.  $f(\alpha)$ ,  $A$ , and  $E$  together make the so-called *kinetic triplet*.

Activation energy is often interpreted as the energy barrier opposing the reaction and pre-exponential or frequency factor as a measure of the probability that a molecule having  $E$  will participate in the reaction. Since  $E$  is associated with the energy barrier, it is suggested that prior to any kinetic analysis, one should investigate the complexity of the process by determining the dependence of  $E$  on  $\alpha$  by isoconversional methods.<sup>12</sup> More details could be found in published papers.<sup>13,14</sup> Because it can deviate from the intrinsic activation energy of a certain individual stage, the experimentally determined  $E$  is commonly termed the *apparent* or *global* activation energy.<sup>12</sup> In this work, isoconversional integral Flynn–Wall–Ozawa (FWO) and differential Friedman (FR) methods were applied. FWO method is based on Eq. (3):

$$\log \beta = \log \frac{AE}{R \cdot g(\alpha)} - 2.315 - 0.4567 \frac{E}{RT} \quad (3)$$

and the FR method is based on Eq. (4):

$$\ln\left(\beta \frac{d\alpha}{dT}\right) = \ln A + \ln f(\alpha) - \frac{E}{RT} \quad (4)$$

The plots  $\log \beta$  vs.  $1/T$ , and  $\ln(\beta d\alpha/dT)$  vs.  $1/T$  obtained at constant  $\alpha$  from  $\alpha$ - $T$  curves recorded at several heating rates should be straight lines, whose slopes allow calculation of  $E$  by means of FWO and FR method, respectively.

## 4. Results and discussion

### 4.1 Re-extrusion

In practice, single or twin-screw extruders could be used for the PET recycling processes. Owing to their high mixing ability, twin-screw extruders are usually utilised in compounding and reactive polymer processing. On the other hand, PET recycling involves no chemical reaction, and thus, single-screw extruders have the advantage over twin-screw extruders due to their lower capital cost, despite their relatively poor mixing ability. This is probably the main reason why they are so widely used in the plastic industry.<sup>15</sup>

In this work, post-consumer PET bottles were gathered, separated entirely from cap and label, and re-extruded in single-screw extruder. The result of this process is shown in Fig. 1. These samples were used for further characterisation.

### 4.1 Fourier transform infrared spectroscopy

In this paper, FTIR analysis was used to evaluate the effect of re-extrusion on the PET structure. FTIR spectra of



Fig. 1 – Post-consumer PET bottle raw material and re-extruded PET samples used for analysis in this work

Slika 1 – Uzorci polaznog materijala PET otpadne boce i reekstrudiranog PET-a upotrijebljeni za analizu u ovom radu

post-consumer PET bottle and re-extruded PET are shown in Fig. 2. The typical absorption bands of PET are well described in the literature.<sup>16–18</sup> Since the melting of PET at elevated temperatures could initiate changes in its structure and consequently the depolymerisation, it is very important to notice the characteristic clues. In that sense, a decrease in the intensity of four characteristic IR vibrational bands (C=O at wavenumber 1714, asymmetric C–O–O stretching at 1242, asymmetric O–C–C stretching at 1095, and CH<sub>2</sub> wagging of the aromatic structure at 723 cm<sup>-1</sup>) with extended contact time and the higher contact temperature should be observed.<sup>19</sup> The formation of hydroxyl groups (3431 cm<sup>-1</sup>) should also be noticed as the result of depolymerisation.<sup>7</sup>

However, no significant difference between FTIR spectra of PET post-consumer bottle and that of the re-extruded PET could be noticed, as shown in Fig. 2. Therefore, it can be concluded that the conditions of re-extrusion process (temperature and screw speed) were mild enough and had

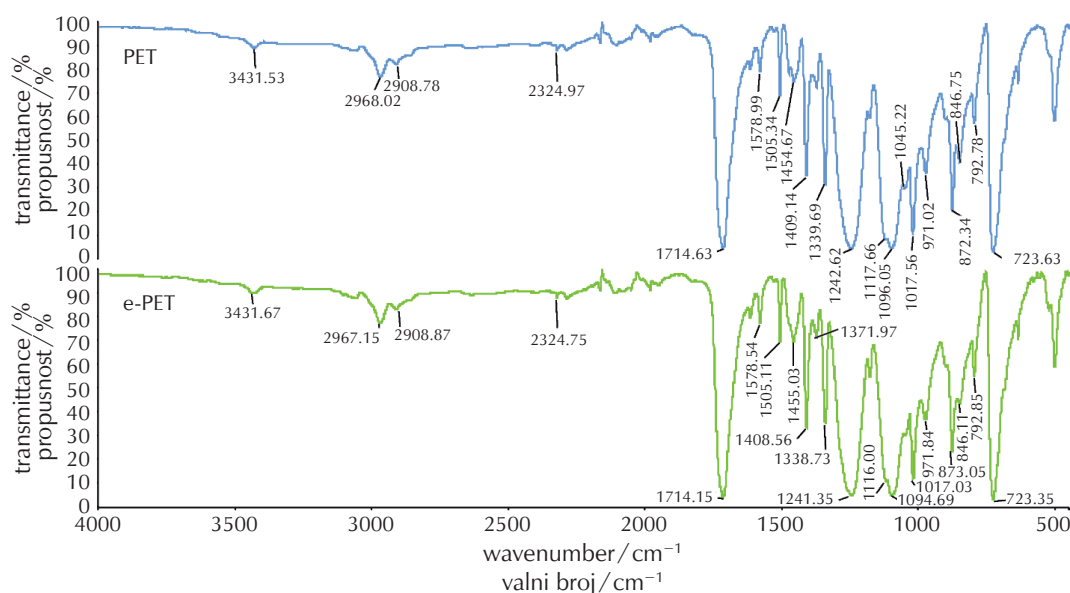


Fig. 2 – FTIR spectra of PET post-consumer bottle and re-extruded PET samples

Slika 2 – FTIR spektri uzoraka PET otpadne boce i reekstrudiranog PET-a

caused no changes in the e-PET structure in comparison to post-consumer PET bottle. These observations are in agreement with the work of *Montaudo et al.*<sup>20</sup>, who studied the degradation products of PET at processing temperatures (270–370 °C). By using MALDI spectrometry, the authors proposed the degradation mechanism and reported that the main degradation products were cyclic oligomers, which only opened and degraded after prolonged exposure to temperatures greater than 370 °C. *Jiang et al.*<sup>21</sup> obtained significant difference between recycled and original PET samples visible in shift and intensity of the absorption peaks. They attributed it to the impurities,<sup>21</sup> but it is more likely this was the result of the degradation process which lowered the PET concentration in the sample.<sup>22</sup> None of that happened in the current investigation.

#### 4.2 Differential scanning calorimetry

As mentioned previously, PET is a semicrystalline thermoplastic polyester widely used in the manufacture of fibres and disposable soft-drink bottles. On the other hand, due to the reversible character of the esterification reaction, polyesters can degrade during processing (extrusion), bottle manufacturing, or recycling (re-extrusion), especially in the presence of moisture. During this type of degradation, the polymer backbone is partly broken, and residual polymer chains with shorter chain length are generated.<sup>23</sup> The consequence of these reactions can be detected by DSC measurement that are shown in Fig. 3 as normalised DSC curves. In this work, the crystallisation of re-extruded PET from the melt took place at significantly higher temperatures (Table 1), unlike the data obtained by *Jiang et al.*,<sup>21</sup> who obtained significantly lower value of  $T_{mc}$  for recycled PET compared to original PET material. They claimed lower crystallisation temperatures of recycled PET, while in this case, e-PET had higher crystallisation temperatures. The smaller polymer chains, produced by degradation during processing, can induce earlier crystallisation from the melt because of their better mobility. The initial nucleation or primary nucleation will start earlier followed by a growth process. *Torres et al.*<sup>24</sup> proved that the degradation products in the recycled PET sample had the role of nucleating agents that facilitated crystallisation. *Mancini and Zanin*<sup>25</sup> investigated degradation, crystallinity (DSC), hardness, tensile and flexural properties of the bottle grade virgin PET through five consecutive injection-moulding steps to simulate recycling. Their results clearly indicated the presence of broken chains, and those small chains mixed with large ones resulted in enhanced mobility, and thus, easier folding of chains in the crystal lattice (lamella), which was then reflected in increased crystallinity of recycled PET. Thermal transition parameters,  $T_g$  and  $T_m$ , determined from the second heating cycle are shown in Table 1.

The DSC curve of post-consumer PET bottle, as well as DSC curve of re-extruded PET, showed one glass transition temperature. Since the glass transition temperature depicted as  $T_{mg}$  is considered the most relevant parameter, it can be concluded that the glass transition temperature of e-PET was not affected by re-extrusion. The same results were obtained by *Torres et al.*<sup>24</sup> The DSC heating curve of PET (Fig. 3) also showed one endotherm, which represents the melting of the crystal phase. However, after re-extrusion,

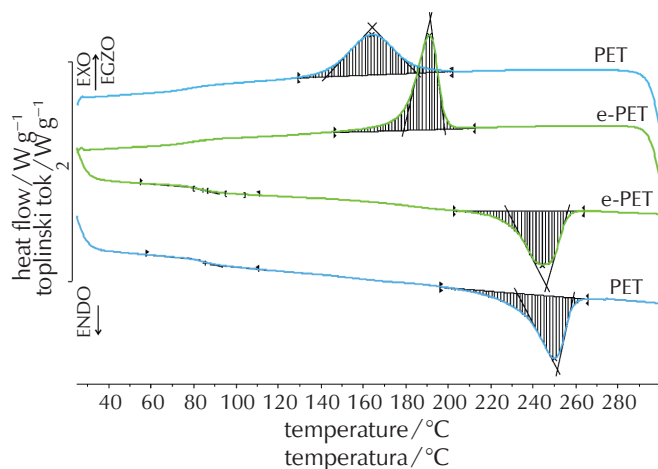


Fig. 3 – Normalised DSC curves of PET post-consumer bottle and re-extruded PET samples

Slika 3 – Normalizirane DSC krivulje uzoraka PET otpadne boce i reekstudiranog PET-a

corresponding melting parameters of e-PET were slightly lower in comparison to the post-consumer PET bottle (Table 1). *Jiang et al.*<sup>21</sup> obtained the same reduction of melting temperature for recycled PET, while *Torres et al.*<sup>24</sup> obtained the opposite trend. Both groups of authors connected their conclusions with the crystallisation process and its influence on the melting process. Having in mind the earlier start of crystallisation from the melt and slightly lower values of  $T_g$  and  $T_m$  of e-PET, it is evident that shorter polymer chains are present in a smaller amount. *Jiang et al.*<sup>21</sup> also concluded that this is the indication of residual shorter polymer chains present in the recycled samples, but the change in their case was much more intense.<sup>21</sup> Also, in the

Table 1 – Thermal transition parameters determined from DSC analysis

Tablica 1 – Značajke toplinskih prijelaza određene iz DSC krivulja

Parameter Značajka		Sample / Uzorak	
		PET	e-PET
$T_g / ^\circ\text{C}$	$T_{eig}$	79	77
	$T_{mg}$	85	85
	$T_{efg}$	91	94
$\Delta C_p / \text{J g}^{-1} \text{ } ^\circ\text{C}^{-1}$		0.20	0.18
$T_m / ^\circ\text{C}$	$T_{eim}$	232	228
	$T_{pm}$	249	244
	$T_{efm}$	258	256
$\Delta H_m / \text{J g}^{-1}$		35.3	30.9
$T_c / ^\circ\text{C}$	$T_{eic}$	185	199
	$T_{pc}$	165	192
	$T_{efc}$	143	179
$\Delta H_c / \text{J g}^{-1}$		31.0	35.6
$X_c / \%$		26	23

case of Jiang *et al.*<sup>21</sup>, the depression of melting temperature was followed by the appearance of the small shoulder on the main melting peak, indicating the presence of smaller or defected crystallites that undergo reorganisation together with the depression of main melting peak.

On the other hand, the degree of crystallinity of e-PET calculated according to Eq. (1) is 23 %, which is slightly lower in comparison to PET (26 %) (Table 1), but insignificant if the experimental error is taken into account. Crystallinity of PET strongly affects the end-use application, and mainly depends on the molecular structure and crystallisation conditions. The decrease in crystallinity could be due to the chain entanglements.<sup>15</sup> Having in mind FTIR measurement that showed no significant change of e-PET structure compared to the PET sample, it can be concluded that recycling of PET with single-screw extruder, at somewhat lower temperature, supports lower mechanical recycle costs and its less negative influence on the environment. The small indication of PET degradation during recycling that was noticed with DSC measurement had to be clarified with TG analysis.

#### 4.3 Thermogravimetric analysis

The comparison of the TG and corresponding DTG curves of investigated samples, obtained at  $10\text{ °C min}^{-1}$ , are shown in Fig. 4. In order to evaluate the effect of re-extrusion on the degradation pattern and consequently on the thermal stability of PET, TG/DTG characteristics were tabulated (Table 2). The post-consumer PET bottle sample degraded through a single degradation stage starting at  $415\text{ °C}$  ( $T_{\text{onset}}$ ) with a  $T_{\text{max}}$  at  $438\text{ °C}$ , leaving a char residue of 16.9 %. Thermal degradation of the e-PET proceeded also through a single degradation stage starting practically at the same temperature with 17.8 % of residue.

Via TG and thermal volatilisation analysis under vacuum, Turnbull *et al.*<sup>26</sup> investigated thermal degradation chemistry of poly(ethylene naphthalate) and compared it to PET. They concluded that PET thermally degrades above temperatures of  $365\text{ °C}$ , subsequently leading to the release of volatile species. Turnbull *et al.* divided those species into condensable (mainly PET oligomers, terephthalic acid, and a number of mono- and di-substituted chain fragments constituting acidic, aldehydic, ester, and vinyl functional

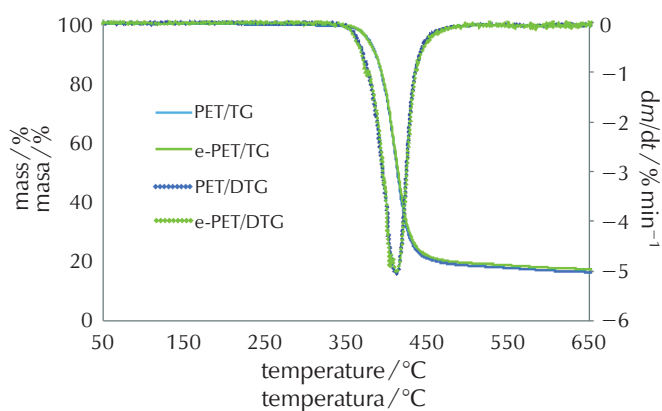


Fig. 4 – Comparison of TG and DTG curves of PET post-consumer bottle and re-extruded PET samples at the heating rate of  $10\text{ °C min}^{-1}$

Slika 4 – Usporedba TG i DTG krivulja uzoraka PET otpadne boce i reekstrudiranog PET-a pri brzini zagrijavanja od  $10\text{ °C min}^{-1}$

groups), and volatile degradation species (carbon dioxide, ethylene, acetylene, acetaldehyde, toluene, benzene, water, benzaldehyde, and benzoic acid), respectively. The authors finally concluded that the predominant reaction in the thermal degradation of PET is the homolytic bond scission of the polymer backbone.

Therefore, mass loss of PET and e-PET in the temperature range of  $350\text{--}550\text{ °C}$  was attributed to the chain scission of the ester bonds. Finally, by data from Table 3 and TG/DTG curves from Fig. 4, it can be concluded that there was no major difference in thermal stability of re-extruded PET sample compared to the post-consumer PET bottle. According to Jiang *et al.*<sup>21</sup>, recycled PET had inferior thermal stability compared to the original PET sample due to some impurities and oligomers produced from PET degradation during recycling process. Evidently, this was not the case in the current investigation, which additionally proved that the selected recycling procedure was appropriate. Thermogravimetric analysis is a powerful analytical tool, and when coupled with other instrumental techniques, such as mass spectrometers and infrared spectrometers, could be additionally used to analyse if degradation of e-PET sample really happened. However, what about the thermal degra-

Table 2 – Characteristics of thermal degradation curves of the samples at heating rate of  $10\text{ °C min}^{-1}$

Tablica 2 – Karakteristike krivulja toplinske razgradnje uzoraka pri brzini zagrijavanja od  $10\text{ °C min}^{-1}$

Sample Uzorak	$\beta/\text{°C min}^{-1}$	$T_{5\%}/\text{°C}$	$T_{\text{onset}}/\text{°C}$	$T_{\text{max}}/\text{°C}$	$R_{\text{max}}/\text{°C min}^{-1}$	$\Delta m/\%$	$m_f/\%$
PET	2.5	376	388	411	5.1	83.8	16.2
	5.0	390	402	425	10.1	83.3	16.7
	10.0	406	415	438	20.6	83.1	16.9
e-PET	2.5	376	389	413	5.0	83.0	16.8
	5.0	390	399	425	9.4	82.8	17.2
	10.0	402	414	433	20.2	82.2	17.8

dation mechanism? Did re-extrusion affect the activation energy of the thermal degradation of recycled PET? The proper kinetic analysis should provide the answer to this question.

#### 4.4 Nonisothermal degradation kinetic analysis

The complexity of the nonisothermal degradation of PET samples in this work was evaluated by the dependence of  $E$  on  $\alpha$ , as presented in Fig. 5. It was clear that the activation energy depended on the conversion in the entire conversion range for both investigated samples, indicating a complex degradation mechanism.

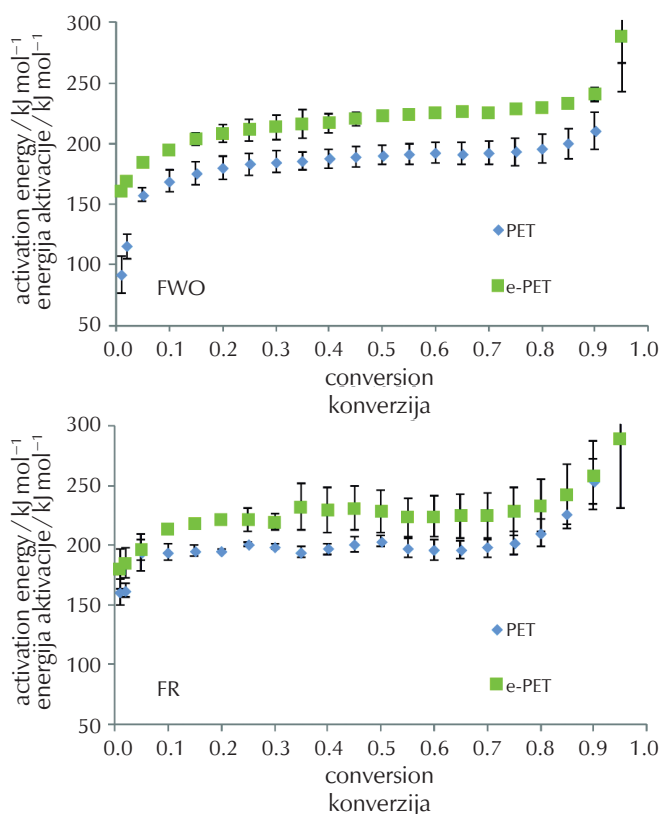


Fig. 5 – Activation energy as a function of degree of conversion for PET post-consumer bottle and re-extruded PET samples calculated by means of Flynn-Wall-Ozawa and Friedman method

Slika 5 – Energija aktivacije u ovisnosti o stupnju konverzije za uzorke PET otpadne boce i reekstrudiranog PET-a, izračunate putem Flynn-Wall-Ozawa i Friedman metode

However, one could also conclude that the degradation pattern of the post-consumer PET bottle sample was practically identical to that of the re-extruded sample. The only major difference between these two samples were the values of the apparent activation energies. Namely, the e-PET sample showed higher values than the PET sample (Table 4). What does this mean in terms of re-extrusion process? In theory, higher activation energy means that

more heat (energy) needs to be delivered to the sample in order for degradation to occur, or in the case of PET, homolytic bond scissions in the polymer backbone. Higher activation energies for the e-PET could be explained by the crystallinity effect. The presence of mixed small and large chains resulted in an easier folding of chains in the crystal lattice (lamella), which increased structure order and density.<sup>25</sup> Finally, this is a good argument in favour of PET bottle recycling, since the material thus obtained was similar to the material obtained from virgin resin. From the computational standpoint, the purpose of kinetic analysis of thermally stimulated processes is to establish mathematical relationships between the process rate, the extent of conversion, and the temperature.<sup>12</sup> This can be accomplished by determining a kinetic triplet. Hence, in order to fully describe the kinetic process of thermal decomposition of PET samples (future research), it was necessary to calculate the other components of kinetic triplet ( $A$  and  $f(\alpha)$ ).

Table 4 – Average values of apparent activation energies obtained by FWO and FR method in the entire conversion range

Tablica 4 – Prosječne vrijednosti energija aktivacije izračunate pomoću FWO i FR metode u cijelom području konverzije

Method Metoda	Conversion range Područje konverzije	$E/kJ mol^{-1}$	
		PET	e-PET
FWO	0.01–0.10	148	183
	0.10–0.80	191	221
	0.80–0.99	239	254
FR	0.01–0.10	162	187
	0.10–0.80	199	225
	0.80–0.99	285	256

## 5 Conclusion

In order to achieve the main goals of this work, post-consumer PET bottles were gathered, manually separated completely from other materials, and re-extruded in a single-screw extruder. Infrared spectroscopy showed no significant difference between FTIR spectra of PET post-consumer bottle and that of the re-extruded PET. This unambiguously proves that the conditions of re-extrusion (temperature and screw speed) were mild, and had caused no significant changes in the e-PET structure. DSC analysis revealed that the glass transition temperature of e-PET was not affected by re-extrusion. However, after re-extrusion, e-PET melted at lower temperatures, while crystallisation of re-extruded PET took place at significantly higher temperatures. The post-consumer PET bottle sample, as well as the e-PET sample, degraded through a single degradation stage starting practically at the same temperature. Selected processing conditions gave results in favour of mechanical recycling, which, in this case, had not destroyed structure and thermal properties of PET. One of the main goals of

this work was to calculate the apparent activation energy; this fact separates our investigation from those previous. Based on the dependence of  $E$  on  $\alpha$ , it could be concluded that the degradation pattern of the investigated samples was complex and practically identical for PET and e-PET, with only the difference in the values of the apparent activation energies. Higher activation energies for the e-PET sample is a good argument in favour of PET bottle recycling, since the material thus obtained was similar to the material obtained from virgin resin.

## List of abbreviations

### Popis kratica

PET	– polyethylene terephthalate – poli(etilen-tereftalat)
e-PET	– extruded polyethylene terephthalate – ekstrudirani poli(etilen-tereftalat)
FTIR	– Fourier transform infrared spectroscopy – infracrvena spektroskopija s Fourierovom transformacijom
UATR	– universal attenuated total reflectance – univerzalna totalna prigušena refleksija
DSC	– differential scanning calorimetry – diferencijalna pretražna kalorimetrija
TG	– thermogravimetric analysis – termogravimetrijska analiza
$T_g$	– glass transition temperature – temperatura staklastog prijelaza
$T_m$	– melting temperature – temperatura taljenja
$T_c$	– crystallisation temperature – temperatura kristalizacije
$T_{eix}$	– extrapolated onset temperature – ekstrapolirana početna temperatura ( $x = g, m, c$ )
$T_{mg}$	– midpoint temperature – midpoint temperatura
$T_{px}$	– peak temperature – temperatura u minimumu prijelaza ( $x = c, m$ )
$T_{efx}$	– extrapolated end temperature – ekstrapolirana konačna temperatura ( $x = g, m, c$ )
$\Delta c_p$	– change of the specific heat capacity – promjena specifičnog toplinskog kapaciteta
$\Delta H_m$	– enthalpy of melting – toplina taljenja
$\Delta H_c$	– enthalpy of crystallisation – toplina kristalizacije
$X_c$	– degree of crystallinity – stupanj kristalnosti
$T_{onset}$	– onset temperature – temperatura početka razgradnje
$T_{5\%}$	– temperature at 5 % mass loss – temperatura pri kojoj uzorak izgubi 5 % početne mase
$T_{max}$	– temperature at the maximum degradation rate – temperatura pri maksimalnoj brzini razgradnje

$R_{max}$	– maximum degradation rate – maksimalna brzina razgradnje
$m_f$	– final mass – konačna ostatna masa
$\Delta_m$	– mass loss – gubitak mase za pojedini stupanj razgradnje
$\alpha$	– degree of conversion – stupanj konverzije
$\beta$	– linear heating rate – linearna brzina zagrijavanja
$T$	– absolute temperature – apsolutna temperatura
$R$	– general gas constant – opća plinska konstanta
$t$	– time – vrijeme
$A$	– pre-exponential factor – predeksponencijalni faktor
$E$	– activation energy – energija aktivacije
$f(\alpha)$ and $g(\alpha)$	– reaction model – reakcijski model

## References

### Literatura

1. T. S. Gomes, L. L. Y. Visconte, E. B. A.V. Pacheco, Life cycle assessment of polyethylene terephthalate packaging: An overview, *J. Polym. Environ.* **29** (2019) 533–548, doi: <https://doi.org/10.1007/s10924-019-01375-5>.
2. J. Nakatani, M. Fujii, Y. Moriguchi, M. Hirao, Life-cycle assessment of domestic and transboundary recycling of post-consumer PET bottles, *Int. J. Life Cycle Assess.* **15** (2010) 590–597, doi: <https://doi.org/10.1007/s11367-010-0189-y>.
3. URL: <https://www.fzoeu.hr/en/packaging-and-packaging-waste-fee/1407> (28. 3. 2022.)
4. Z. O. G. Schyns, M. P. Shaver, Mechanical recycling of packaging plastics: A review, *Macromol. Rapid Commun.* **42** (2021) 2000415–2000442, doi: <https://doi.org/10.1002/marc.202000415>.
5. J. Maris, S. Bourdon, J. M. Brossard, L. Cauret, L. Fontaine, V. Montembault, Mechanical recycling: Compatibilization of mixed thermoplastic wastes, *Polym. Degrad. Stab.* **147** (2018) 245–266, doi: <https://doi.org/10.1016/j.polymdegradstab.2017.11.001>.
6. P. Oblak, J. Gonzalez-Gutierrez, B. Zupančić, A. Aulova, I. Emri, Processability and mechanical properties of extensively recycled high density polyethylene, *Polym. Degrad. Stab.* **114** (2015) 133–145, doi: <https://doi.org/10.1016/j.polymdegradstab.2015.01.012>.
7. Lj. Kratošil Krehula, Recikliranje plastičnog otpada, *Zaštita okoliša, Kem. Ind.* **64** (7-8) (2015) 417–420, <https://hrcak.srce.hr/file/209194>.
8. A. Ptiček Siročić, M. Đurina, E. Špoljarić, Pet packaging recovery, *Inženjerstvo okoliša*, **3** (2016) 83–88, <https://hrcak.srce.hr/162342>.
9. ISO 11357-2: 2009 Plastics-Differential scanning calorimetry (DSC) – Part 2: Determination of glass transition temperature.
10. ISO 11357-3: 2009 Plastics – Differential scanning calorimetry (DSC) – Part 3: Determination of the maximum degradation rate.

- etry (DSC) – Part 3: Determination of temperature and enthalpy of melting and crystallization.
11. D. Loaeza, J. Cailloux, O. Santana Pérez, M. Sánchez-Soto, M. L. Maspocho, Impact of titanium dioxide in the mechanical recycling of post-consumer polyethylene terephthalate bottle waste: Tensile and fracture behavior, *Polymers* **13** (2021) 310–326, doi: <https://doi.org/10.3390/polym13020310>.
  12. S. Vyazovkin, A. K. Burnham, J. M. Criado, L. A. Pérez-Maque-da, C. Popescu, N. Sbirrazzuoli, ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data, *Thermochim. Acta* **520** (2011) 1–19, doi: <https://doi.org/10.1016/j.tca.2011.03.034>.
  13. M. Erceg, I. Krešić, N. Stipanelov Vrandečić, M. Jakić, Different approaches to the kinetic analysis of thermal degradation of poly(ethylene oxide), *J. Therm. Anal. Calorim.* **131** (2018) 325–334, doi: <https://doi.org/10.1007/s10973-017-6349-6>.
  14. M. Erceg, M. Jakić, I. Krešić, Utjecaj istraživača na rezultate kinetičke analize toplinske razgradnje polimera, *Kem. Ind.* **69** (9-10) (2020) 493–502, doi: <https://doi.org/10.15255/KUI.2020.044>.
  15. F. Awaja, D. Pavel, Recycling of PET, *Eur. Polym. J.* **41** (2005) 1453–1477, doi: <https://doi.org/10.1016/j.eurpolymj.2005.02.005>.
  16. S. Vijayakumar, P. R. Rajakumar, Infrared spectral analysis of waste pet samples, *Int. Lett. Chem. Phys. Astron.* **4** (2012) 58–65, doi: <https://doi.org/10.18052/www.scipress.com/IL-CPA.4.58>.
  17. A. P. dos Santos Pereira, M. H. Prado da Silva, É. Pereira Lima Júnior, A. dos Santos Paula, F. J. Tommasini, Processing and characterization of PET composites reinforced with geopolymer concrete waste, *Mat. Res.* **20** (2017) 411–420, doi: <https://doi.org/10.1590/1980-5373-MR-2017-0734>.
  18. Z. Chen, J. N. Hay, M. J. Jenkins, The thermal analysis of poly(ethylene terephthalate) by FTIR spectroscopy, *Thermochim. Acta* **552** (2013) 123–130, doi: <https://doi.org/10.1016/j.tca.2012.11.002>.
  19. M. Forrest, Recycling of polyethylene terephthalate, Smithers Rapra Technology Ltd, Shawbury, Shrewsbury, Shropshire, United Kingdom, 2016.
  20. G. Montaudo, C. Puglisi, F. Samperi, Primary thermal-degradation mechanisms of PET and PBT, *Polym. Degrad. Stab.* **42** (1993) 13–28, doi: [https://doi.org/10.1016/0141-3910\(93\)90021-A](https://doi.org/10.1016/0141-3910(93)90021-A).
  21. Z. Jiang, Z. Guo, Z. Zhang, Y. Qi, C. Pu, Q. Wang, Z. Jia, C. Xiao, Preparation and properties of bottle-recycled polyethylene terephthalate (PET) filaments, *Text. Res. J.* **89** (2018) 1207–1214, doi: <https://doi.org/10.1177/0040517518767146>.
  22. Lj. Kratofil Krehula, Z. Hrnjak-Murgić, B. Andričić, J. Jelenčić, Study of PET depolymerization during recycling, *e-Polymers* **8** (2008) 089, doi: <https://doi.org/10.1515/epoly.2008.8.1.1039>.
  23. R. Francis, Recycling of Polymers: Methods, Characterization and Applications, Wiley-VCH, Weinheim, Germany, 2017, doi: <https://doi.org/10.1002/9783527689002>.
  24. N. Torres, J. J. Robin, B. Boutevin, Study of thermal and mechanical properties of virgin and recycled poly(ethylene terephthalate) before and after injection molding, *Eur. Polym. J.* **36** (2000) 2075–2080, doi: [https://doi.org/10.1016/S0014-3057\(99\)00301-8](https://doi.org/10.1016/S0014-3057(99)00301-8).
  25. S. D. Mancini, M. Zanin, Recyclability of PET from Virgin Resin, *Mat. Res.* **2** (1999) 33–38, doi: <https://doi.org/10.1590/S1516-14391999000100006>.
  26. L. Turnbull, J. J. Liggat, W. A. MacDonald, Thermal degradation chemistry of poly(ethylene naphthalate) – A study by thermal volatilisation analysis, *Polym. Degrad. Stab.* **98** (2013) 2244–2258, doi: <https://doi.org/10.1016/j.polymdegradstab.2013.08.018>.

## SAŽETAK

### Recikliranje otpadnih PET boca: utjecaj reekstrudiranja na strukturu, toplinska svojstva i prividnu energiju aktivacije

Miće Jakić,\* Sanja Perinović Jozić, Ivana Bandić i Laura Ključić

U ovom radu prikupljene su otpadne PET (poli(etilen-tereftalat)) boce, odvojene od ostalih materijala i reekstrudirane. S ciljem utvrđivanja utjecaja reekstrudiranja na strukturu PET-a primijenjena je infracrvena spektroskopija s Fourierovom transformacijom. Nije utvrđen značajan utjecaj procesa reekstrudiranja na strukturu PET-a. Uzorci su također karakterizirani primjenom diferencijalne pretražne kalorimetrije (DSC) s ciljem određivanja karakterističnih toplinskih prijelaza PET-a. Rezultati DSC analize ukazali su na to da se ekstrudirani PET započinje taliti pri nižim temperaturama, odnosno kristalizacija započinje pri znatno višim temperaturama u odnosu na PET. Termogravimetrijska analiza (TG) primijenjena je s ciljem procjene utjecaja reekstrudiranja na toplinsku stabilnost uzoraka. TG analizom potvrđeno je da reekstrudiranje nije utjecalo na toplinsku stabilnost istraživanih PET uzoraka. Konačno, primjenom izokonverzijskih Flynn-Wall-Ozawa i Friedman metoda analize izračunate su energije aktivacije toplinske razgradnje istraživanih uzoraka. U usporedbi s uzorkom PET boce, reekstrudirani PET uzorak pokazuje višu vrijednost energije aktivacije, što je dodatan argument u prilog recikliranja PET boca.

#### Ključne riječi

Poli(etilen-tereftalat), otpadne boce, recikliranje, reekstruzija, toplinska svojstva, energija aktivacije

Sveučilište u Splitu, Kemijsko-tehnološki fakultet, Ruđera Boškovića 35, 21 000 Split

Stručni rad  
Prispjelo 19. listopada 2022.  
Prihvaćeno 1. veljače 2023.