

Preliminary Studies about PET Degradation. Rheological Determinations on Glycolysis Products Obtained with Propylene Glycol

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Abstract: At the global level, consumption of plastic products has increased dramatically over the past few decades. This trend results in the generation of a vast waste stream that needs to be properly managed to avoid environmental damage. Increasingly stringent European legislation is setting new standards that promote the application of new recycling technologies capable of absorbing large amounts of plastic waste. The recycling of post-consumer PET (polyethylene terephthalate) bottles represents one of the most successful and widespread examples of polymer recycling.

The paper presents preliminary studies about chemical recycling of PET wastes through glycolysis and the rheological characterization of the obtained glycolysis products. The chemical agent used for degradation of PET wastes was propylene glycol (PG) in the presence of zinc acetate as transesterification catalyst.

Keywords: polyethylene terephthalate, waste, glycolysis, rheological behaviour

1. Introduction

PET package wastes represent a huge amount of uncollected wastes and consequently unrecycled, producing so-called "pollution by accumulation". In this way, wasting of raw materials and energy, as well as landscape deterioration with PET waste, constitute an aggressive factor for both environment and localities look, conducting therefore at a decrease in time of touristic potential, by uncontrolled storage on the river beds, valleys, localities input and output, along the roads, lines of rails, green area.

Polyethylene terephthalate (PET) has become one of the most valuable recyclable materials which are used especially in the manufacturing of soft drink bottles. It has excellent tensile and impact strength, chemical resistance, clarity, colour ability, processability and reasonable thermal stability [1,2].

PET is a relatively new packaging resin. The PET bottle was patented in 1973 and the first PET bottle was recycled in 1977 [3]. The PET repeating unit is shown in Fig.1.

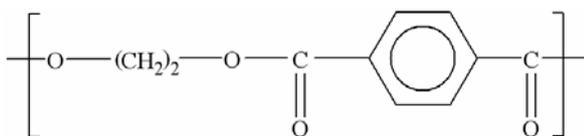


Figure 1. PET repeating unit

The recycling industry of PET waste started as result of environmental pressure to improve waste management, considering that natural decomposition rate of the PET is very slow. PET is a non-degradable plastic in normal conditions, but, in recent years, the interest for biological

degradation has been increased [4,5,6] even complicated and costly procedures are necessary.

The following properties of recycled PET reported by some researchers [2,7] for successful reprocessing are summarized in Table 1.

TABLE 1. Minimum requirements of PET flakes for successful reprocessing

Property	Value
Intrinsic viscosity	> 0.7 dl g ⁻¹
Water content	< 0.02 wt.%
Size of flakes	0.4 mm ÷ 8 mm
Dyes content	< 10 ppm
Yellowing index	< 20
Metal content	< 3 ppm
PVC content	< 50 ppm
Polyolefin content	< 10 ppm

Today, recycling methods for PET package wastes applied to industrial scale at international level are [8]: 1) *recycling with energy recovery* which consists in wastes cremation; 2) *mechanical recycling*, is the most used method for PET recycling consisting in many simples and relative cheap selection, washing and grinding processes of recuperate material; 3) *chemical recycling* of PET post-consumer package wastes imply splitting of the constituent macromolecules of PET package wastes obtaining new products used in chemical and petrochemical industry.

The chemical recycling of post-consumer PET wastes has been the subject of many studies. Chemical degradation can be carried out by different chemical processes: hydrolysis [9-14] using water, acids or alkalis, methanolysis [15,16], glycolysis [17-20] and other methods [21, 22, 23].

This preliminary study focuses on the chemical degradation of PET waste by glycolysis using propylene glycols and the rheological characterization of the glycolysis products. Examination of the rheological properties of glycolysis products is an important step in the characterization and understanding of their properties.

As regards the aspect of the rheological characters, the fluids are divided in two important classes: Newtonians and non-Newtonians. The Newtonian viscous fluid is distinguished through the fact that at simple shear stress, the relation between tangential stress and shear rate is linear. After the solicitation is ceased the fluid remains undistorted. A fluid showing any deviation from the above behaviour is non-Newtonian [24, 25].

2. Experimental

• Glycolysis of PET waste

Post consumer PET drink bottles were cut into small flakes ($2 \div 4 \text{ mm} \times 8 \div 10 \text{ mm}$), cleaned by washing and then were dried.

In the PET glycolysis, 50 g (0.26 mol/repeating unit) of PET waste flakes were added into a reactor together with the glycol in following PET: PG molar ratio: 1:5, 1:4, 1:3, 1:2 and 1:1. The reaction was carried out at 240°C for 4 hours in the presence of zinc acetate (1% by total weight of reaction mixture) as catalyst.

• Rheological characterization of the glycolysis products

The rheological experiments were performed by a rotational viscometer Rheotest RV which functions based on the principle of rotation of a cylinder immersed in the researched probe, measuring the necessary torsion moment to surmount the resistance at rotation due to the sample viscosity. The torque acting on the rotor surface is detected in terms of the degree of the torsion of spring in the viscometer, and the viscosity of the sample is calculated from the dial reading which corresponds to the degree of torsion.

The probes were heated at different temperatures, being maintained constant by thermostat installation of the viscometer. It was been made viscosity determinations at different temperatures and rheological behaviour for obtained glycolysis products was analyzed.

3. Results and discussion

• Viscosity determinations

The influence of temperature on viscosity of the glycolysis products obtained at different molar ratios of the reactant has been studied. The viscosity values were obtained at a constant shear rate for four values of the temperature ($\sim 50^\circ\text{C}$, $\sim 60^\circ\text{C}$, $\sim 70^\circ\text{C}$ and $\sim 80^\circ\text{C}$).

The variation of the glycolysis products viscosity with the temperature is shown in Fig. 2 and Fig. 3.

The changing of the viscosity with the temperature has been investigated by various researchers. There are several viscosity-temperature equations; the most commonly used are given in Table 2 [26].

TABLE 2. Viscosity-temperature equations

Name	Equation	Comments
Reynolds	$\eta = b \cdot e^{-a \cdot T}$	Early equation; accurate only for a very limited temperature range
Slotte	$\eta = \frac{a}{(b + T)^c}$	Reasonable; useful in numerical analysis
Vogel	$\eta = a \cdot e^{\frac{b}{T-c}}$	Most accurate; very useful in engineering calculations

where: a, b, c – constants; η – the dynamic viscosity at the atmospheric pressure [cP] and T – is the absolute temperature [K].

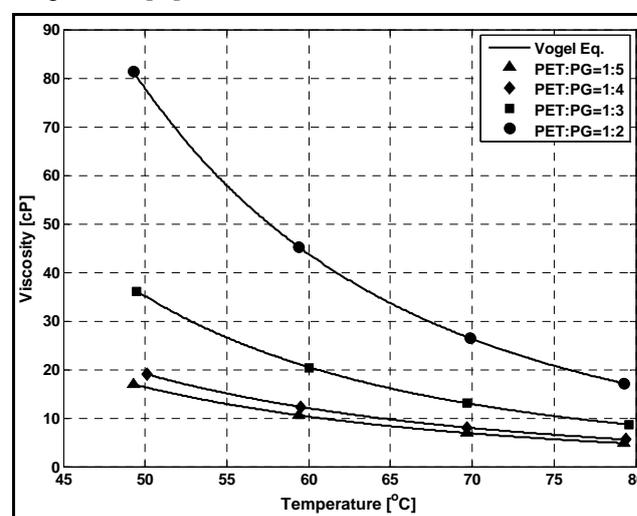


Figure 2. Variation of the glycolysis products viscosity with the temperature

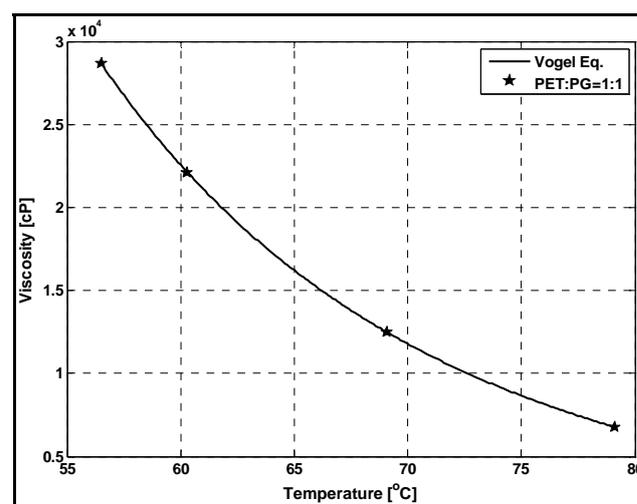


Figure 3. Variation of the glycolysis product viscosity with the temperature

In this study, Vogel equation is used for fit the experimental viscosity data. To find the values of the constants a, b and c was create a MATLAB program which

uses the backlash operator (\backslash). In order to use the backlash operator, was converting the Vogel equation into a linear form:

$$\ln \eta = \ln a + \frac{b - \ln a \cdot c}{T} + \frac{c \cdot \ln \eta}{T} \quad (1)$$

The obtained values for the constants a , b and c from Vogel equation and determination coefficients R^2 is presented in Table 3.

TABLE 3. Constants from Vogel equation

PET:PG molar ratio	a	b	c	R ²
1:5	0.0043849	1382.278	155.04604	0.99993
1:4	0.0040299	1461.366	150.48739	0.99999
1:3	0.0171007	1005.547	191.30500	0.99992
1:2	0.0048115	1535.072	164.75233	0.99999
1:1	2.9973e-4	4880.657	64.048357	0.99999

Similar results can be observed in all presented cases. According to expectations, the viscosity of all glycolysis products decreases with increasing temperature.

It is observed that with decrease of the glycol quantities used in glycolysis process, the viscosity values increases, more pronounced in the case of glycolysis products obtained at PET:glycol = 1:1 molar ratio.

• Flowing behavior

The relationship between the shear stress and shear rate describes the fluids rheological behaviour. The values of the shear stress were calculated based on the viscosity values obtained by increasing shear rate.

For glycolysis products obtained at PET:PG = 1:3 and PET:PG = 1:2 molar ratio, the flow curves, shear stress vs. shear rate, for different temperatures are shown in Fig. 4 and Fig. 5.

In both cases, the flow curves are straight lines passing through the origin, this indicates a Newtonian behaviour.

The relationship between shear stress τ and shear rate $\dot{\gamma}$ is given by the Eq. 2 [27], where the proportionality constant is the viscosity η .

$$\tau = \eta \cdot \dot{\gamma} \quad (2)$$

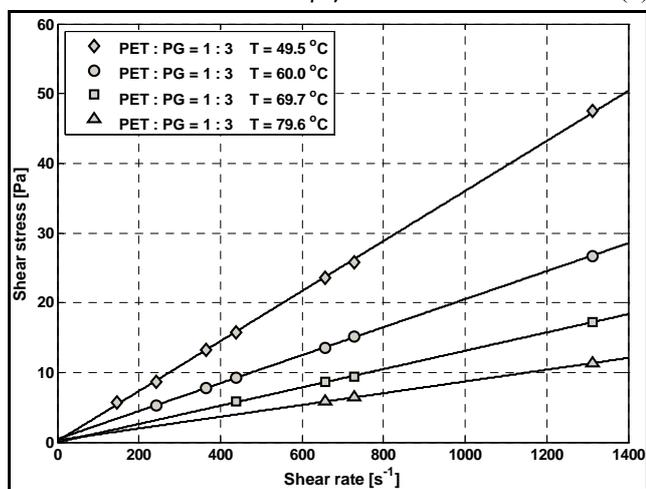


Fig.4. The flowing curves for the glycolysis products obtained at PET:PG = 1:3 molar ratio

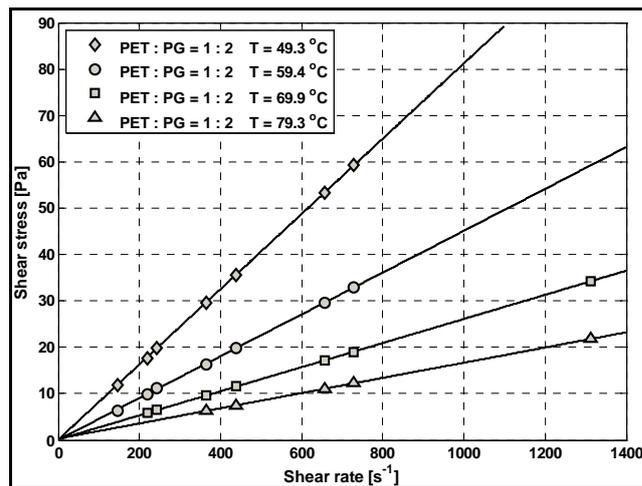


Figure 5. The flowing curves for the glycolysis products obtained at PET:PG = 1:2 molar ratio

For glycolysis products obtained at PET:PG = 1:1 molar ratio, the corresponding flow curves are presented in Fig. 6.

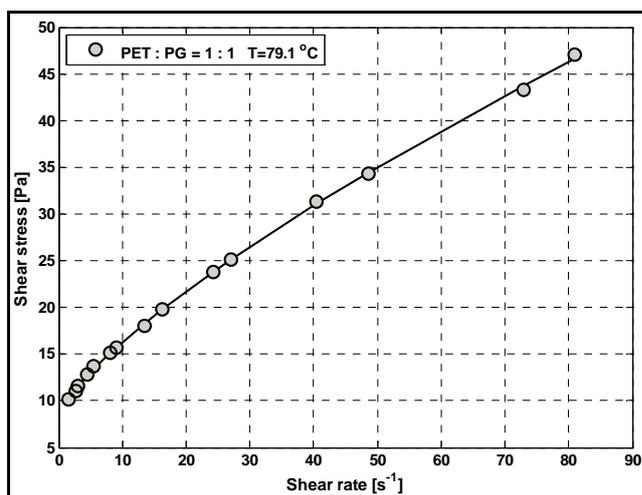


Figure 6. The flowing curves for the glycolysis product obtained at PET:PG = 1:1 molar ratio

The rheological behavior, shear stress vs. shear rate, of this sample showed a non-Newtonian character with a pseudoplastic behaviour. The experimental data were fitted according to Herschel-Bulkley model (also called the generalized Bingham model) [28-30]:

$$\tau = \tau_0 + K \cdot \dot{\gamma}^n \quad (3)$$

where: τ is the shear stress, τ_0 is the yield stress (commonly defined as the stress that is required to initiate flow of the material), $\dot{\gamma}$ is the shear rate, K is the consistency coefficient and n is the flow behavior index. The linearised form of the Herschel-Bulkley model is used to calculate the parameters of the model. Different values for τ_0 are assumed in order to establish the best linear regression judged from the correlation coefficient and the sum of error squares, resulting the intercept ($\ln K$) and the slope (n). Obtained results indicate a very good agreement between experimental values and those calculated with Eq. 3.

The values of parameters obtained for the Herschel-Bulkley model are presented in Table 4.

TABLE 4. Parameters of Herschel-Bulkley model

Parameter	τ_0 [Pa]	K [Pa · s ⁿ]	n	R ²
Value	8.3222515	1.4084804	0.7518575	0.9996

The flow index n can be used to classify the fluids, $n > 1$ indicates a shear-thickening fluid (dilatant behaviour) and $n < 1$ indicates a shear-thinning flow (pseudoplastic behaviour) [31,32].

4. Conclusions

Regarding to the effect of the temperature on viscosity of the glycolysis products, in all studied cases the viscosity increases with growth of temperature value. At high molar ratios the temperature influence on glycolysis products viscosity are not so pronounced than at small molar ratios.

Comparison of experimental viscosities and those calculated with Vogel equation show a very good agreement in all presented cases.

Regarding to the rheological behaviour, glycolysis products obtained with propylene glycol at PET:glycol = 1:2 and 1:3 molar ratio shows a Newtonian character.

For glycolysis products obtained at PET:PG = 1:1 molar ratio, the flowing curves shows a non-Newtonian character with a pseudoplastic behaviour. The Herschel-Bulkley model was used to characterize the behavior of these glycolysis products. The determination coefficients R² were higher than 0.99, denoting that Herschel-Bulkley model fit very well the experimental data.

Future objectives:

- rheological determinations on glycolysis products obtained with dipropylene glycol (DPG), ethylene glycol (EG) and diethylene glycol (DEG) and the comparison between obtained data.
- the characterization of the obtained glycolysis products by Gel Permeation Chromatography, Mass Spectrometry, Scanning Electron Microscopy and Differential Scanning Calorimetry;
- investigation of the catalyst effect and flakes size in PET glycolysis;
- glycolysis of PET waste in other condition of temperature and time in order to optimise process parameters;
- synthesis and characterization of the unsaturated polyester resins and comparing with commercial UPE resins.

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