

# Utilization of Crude Glycerol and Waste Poly(ethylene terephthalate) for Production of Unsaturated Polyester Resins



## Environmental Science

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**Nikola Todorov, Ph.D.**

Technical University "Prof. dr. Asen Zlatarov", Natural Sciences Faculty Ecology and Environmental Protection Department

### ABSTRACT

*Two waste products – crude glycerol (CGly) and waste poly(ethylene terephthalate) (PET) were utilized to obtain unsaturated polyester resins. PET flakes from beverage bottles were subjected to glycolysis at 210°C with CGly obtained as side product of biodiesel production. Two fractions of polyester polyols were separated from the glycolysis product – water soluble (WSF) and water insoluble (WIF). They were further used in a process of polycondensation with propylene glycol and maleic anhydride. The unsaturated polyesters obtained were mixed with styrene and solidified with a suitable system activator-accelerator. Some basic characteristics of the cured products were studied.*

### INTRODUCTION

The recycling of poly(ethylene terephthalate) (PET) is of great ecological and social importance. There are many data in the literature [1-5] about the chemical recycling of PET by glycolysis and the utilization of the glycolysis product to obtain unsaturated polyesters (UPE). Usually, glycolysis is carried out with propylene glycol (PG) or mixtures of PG, ethylene glycol (EG) and diethylene glycol (DEG) [3-5].

However, the data on the glycolysis of PET with glycerol are scarce [6]. Irena Vitkauskienė and Ričardas Makuška[7] carried out glycolysis of industrial PET with EG and DEG. To prevent the crystallization of the products obtained, they added from 1 to 12% glycerol and adipic acid. The polyester polyols obtained were used as precursors for the preparation of UPE.

Other authors [8, 9] implemented glycerol interaction with para formaldehyde [8] or acetic and benzoic acid [9]. The monohydric acetal [8] or mono- and diacetate [9] of glycerol were then subjected to interaction with propylene glycol and maleic anhydride to produce UPE.

There are no data in the literature on glycolysis of PET with crude glycerol obtained as side product from biodiesel production. Besides, there are no data on the use of the polyester polyols obtained as precursors for the preparation of unsaturated polyester resins which is the aim of the present study.

## 2. MATERIALS AND METHODS

### 2.1. Materials

PET flakes were obtained from beverage bottles. Crude glycerol was purchased on the market. Propylene glycol, xylene, maleic anhydride (MA), phthalic anhydride (PhA) were of grade pure for analysis. KOH, toluene, Pb acetate and Co naphthenate, methylethyl ketone peroxide (MEKP) were purchased from Aldrich.

### 2.2. Glycolysis of PET

In a round bottom flask of 1.0L equipped with stirrer, Dean-Stark apparatus, thermometer and inert gas inlet, 180 g CGly (1,6 mol Gly) and 18 g toluene were placed. The stirrer was switched on and the mixture was heated to 120°C until full evaporation of the water contained in it. Then 76,8 g (0,4 mol) preliminarily heated flakes of waste PET were added and the temperature was raised to 210°C. The glycolysis was carried out at atmospheric pressure for 150 min.

The whole content of the reactor was poured into hot distilled water. The solution was hot filtered and cooled down to 4°C for 8 hours. The white precipitate obtained was purified, dried in vacuum at 40°C and labeled water-soluble fraction (WSF). The product which did not dissolve in hot water was washed, dried and labeled water-insoluble fraction (WIF).

### 2.3. Synthesis of unsaturated polyesters

The initial reagents were placed in a flask of 500 ml equipped with stirrer, Dean-Stark apparatus, thermometer and inert gas inlet. For UPE-1 these were 41,1 g (0,1 mol) WSF, 38 g (0,5 mol) propylene glycol and 49 g (0,5 mol) maleic anhydride.

The process started at temperature of 130°C and it was gradually raised by rate of 10°C per hour to 190 °C and then kept at this temperature until acid number of less than 50 mg KOH/g was measured. The polyesters obtained were cooled to 120°C and 0,02 wt.% hydroquinone in 0,2 ml ethanol were added. The system was left in vacuum for one more hour to remove the easily volatile components.

The following unsaturated polyesters were obtained by the same method:

- ♦ UPE-2 from 38,1 g (0,04 mol) WSF, 30,4 g (0,4 mol) PG and 39,2 g (0,4 mol) MA and
- ♦ UPE-3 from 53,2 g (0,7 mol) PG, 36 g (0,37mol) MA and 35 g (0,23 mol) PhA.

### 2.4. Solidification of the unsaturated polyester resins

At temperature of 70°C, styrene was added to the unsaturated polyesters and the mixture was homogenized. To initiate solidification, 2 wt.% 6 % phthalate solution of CoNp and 1% MEKP were added as 50% phthalate solution as accelerator and initiator, respectively. The compositions were cast in preliminarily prepared pots. The curing was carried out at temperature of 35°C for 12 h, then the temperature was increased to 85°C for 1 h, followed by postcure for 2 hours at 110°C.

### 2.5. Analysis and characterization

- **Acid number** – determined according to EN 14104:2003.
- **Analysis of Gly** – The contents of glycerol, water and ashes were determined according to the standards EN 14106:2003, EN ISO 12937:2003 and ISO 3987:1999, respectively.
- **Viscosity** – determined according to DIN 53211 -4, 60% butylacetate solution.
- **Mechanical Testing** was performed at 25±2°C, using a *Instron* 5866 Testing Instrument, according to ASTM D638 and ASTM D790.
- **Indentation hardness** was measured with GYZJ 934-1 Barcol impressor according to ASTM D 2583-99.
- **DSC** – analyses were carried out on an apparatus: „STA – TG-

DSC/DTA F3 JUPITER™ product of NETZSCH – Germany, in the temperature interval from 20 to 650°C in nitrogen atmosphere.

- **GPH-** The measurements were taken using the system WATERS consisting of M510 pump, U6K injector, refractometric detector M410 and UV detector M484, at flow rate of 1.0 ml/min, temperature 40°C, THF solvent. The molecular mass characteristics were determined using polystyrene standards and CLARITY software.

- **<sup>1</sup>H NMR** – The spectra were registered on a spectrophotometer Bruker Avance II+ 600 in acetone solution. TMS was used as internal standard for the chemical shifts ( $\delta$ , ppm).

## RESULTS AND DISCUSSION

The two types of unsaturated polyesters prepared in the present work differ from the ones known from the literature by the fact that they were obtained by simultaneous utilization of two waste products – PET from beverage bottles and crude glycerol – a side product from biodiesel production. To produce unsaturated polyesters, the following 4 stages were necessary: glycolysis of PET, separation of WSF and WIF, synthesis of unsaturated polyesters and solidification of unsaturated polyester resins.

### • Glycolysis of waste PET with crude glycerol

Some basic characteristics of the waste PET and CGly were determined. The DSC studies showed that the temperatures of glass transition  $T_g$  and melting  $T_m$  of the waste PET were 87.9 and 248.6°C, respectively while for the fresh PET  $T_g$  is 72°C and  $T_m$  is 253°C. These changes can be explained with the processes of oxidation and destruction taking place in PET.

The composition of the crude glycerol was determined by standard methods /see 2.5/. The glycerol content was found to be 81.5%, water – 8.7% and ashes – 6.6%. The content of matter organic non-glycerol /MONG/ was calculated from the difference: (100 - (% glycerol content +% water content +% ashes content)). Crude glycerol was brown by colour. The analysis of the ashes revealed that it was  $\text{Na}_2\text{SO}_4$ .

The glycolysis of the waste PET with the crude glycerol was carried out as described in section 2.2, at molar ratio CGly/PET = 4. It is important to note that no catalyst was used for the process. It is well known [1-7] that salts of heavy metals are usually used as catalysts of the glycolysis. In the present work, the process was accelerated by the  $\text{Na}_2\text{SO}_4$  present in the crude glycerol as impurity. Besides, the temperature was kept about 200-210°C during the entire process so the secondary OH groups if the glycerol remained inactive.

### • Separation and analysis of WSF and WIF

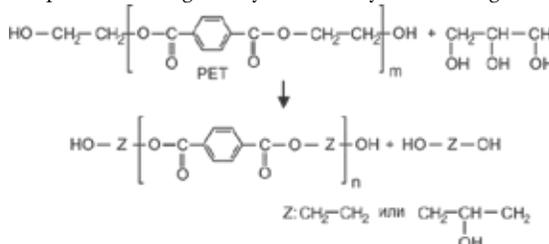
The glycolysis product is a complex mixture of polyester polyols of various molecular weights, free glycerol, ethylene glycol,  $\text{Na}_2\text{SO}_4$ , MONG and pigments. Polyester polyols were separated from the mixture thanks to their water solubility difference – 4°C for the WSF and 90°C for WIF (method described in section 2.2). The rest of the mixture components can be used again in PET glycolysis after evaporation of the water.

Some basic characteristics and the structures of the two fractions were studied by DSC, GPH and <sup>1</sup>H NMR. It was found that WSF was a solid white product with melting temperature 125.1°C and number average molecular weight 411g mol<sup>-1</sup>. WIF was white product with melting temperature 172.5°C and number average molecular weight 953g mol<sup>-1</sup>

In the <sup>1</sup>H NMR spectrum of WSF, two quartets were observed in the intervals 3.713-3.806 ppm and 4.386 – 4.507 ppm for the chemical shifts of the protons in the  $\text{CH}_2\text{COO}$  and  $\text{CH}_2\text{OH}$

groups, respectively. The integral intensity of the signal at  $\delta$  5.263 showed that only 12% of the glycerol units interacted with the secondary OH group which may lead to branched structure or cyclization. It means that the bonding of the glycerol units in the depolymerized molecules occurred mainly at the expense of the primary OH groups. This was confirmed by the high hydroxyl number which was 490 mg KOH/g for WSF and 953 mg KOH/g for the WIF. In such cases, the depolymerization with glycerol can be called glycolysis [6].

The process can be generally described by the following scheme:



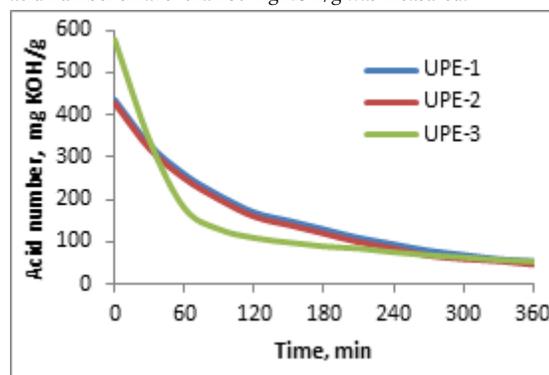
**Scheme 1. Glycolysis of PET with glycerol**

Signals at  $\delta$  3.90 ppm were observed in the <sup>1</sup>H NMR spectrum. They can be attributed to the methylene protons in the  $\text{CH}_2\text{-O-CH}_2$  groups and proved the occurring of processes of esterification, i.e. formation of Z-O-Z bonds as shown in Scheme 1. Although small by number (9%), these bonds are important since they impart flexibility to oligomer molecules.

It is important to note also that both the crude glycerol and glycolysis product were brown colored but the individual fractions were white.

### • Synthesis and study of the unsaturated polyesters.

A total of three unsaturated polyesters were synthesized by the method described in section 2.3. UPE-1 was obtained by polycondensation of WSF, propylene glycol and MA. It was calculated that about 34 wt.% of the necessary initial monomers were introduced with the WSF. For the synthesis of UPE-2, 36 wt.% of the necessary monomers were introduced with the WIF. UPE-3 was prepared by polycondensation of PG, MA and PhA, as reference. In all the compositions used, the molar ratio glycols/anhydrides in the initial mixtures was 1,1. The polycondensation was monitored by measuring the change of the acid number /Fig.1/. It can be seen from the figure that the process rate was high until about 100<sup>th</sup> minute for the three types of polyesters and then sharply decreased. This can be explained with the increase of the consistency and approach of the process of polycondensation to equilibrium. The polyesterification was carried out until acid number smaller than 50 mg KOH/g was measured.



**Fig.1. Change of acid number with time for the preparation of UPE-1, UPE-2 and UPE-3**

Some basic characteristics of the polyesters obtained were determined (Table 2).

**Table 2. Basic characteristics of the unsaturated polyesters**

Characteristic	UPE-1	UPE-2	UPE-3
Appearance	Transparent syrupy liquid	Transparent syrupy liquid	Transparent syrupy liquid
Density at 20°C, g/cm <sup>3</sup>	1,241	1,244	1,194
Solvents	Acetone, THF, xylene	Acetone, THF, xylene	Acetone, THF, xylene
Relative viscosity, Ø4 mm/ (20±0,5)°C, s	275	293	240
Compatibility with monostyrene, wt %	31	31	>40
Number average molecular weight	2640	3150	2210
Gardner colour	3	3	3

It can be seen that the basic characteristics of UPE-1 and UPE-2 are quite close to these of the reference polyesters - UPE-3. The main difference is in the molecular weight which probably affects the viscosity.

#### • Solidification of the unsaturated polyester resins.

All the unsaturated polyester resins were obtained by mixing them with 30% styrene. The solidification was carried out by the method described in section 2.4 and their Barcol hardness, compression and tensile strengths were studied. It was found that:

- Barcol hardness – 47 for UPE-1, UPE-2 and for UPE-3.
- Flexural strength – 43 and 45 MPa for UPE-1 and UPE-2 respectively and 40 MPa for UPE-3.
- Tensile strength – 28,4 and 28,6 MPa for UPE-1 and UPE-2 respectively and 28,1 for UPE-3.

The results obtained showed that the solidified products containing WSF or WIF had better tensile and flexural strength and the hardness did not deteriorate. This can be explained with the presence of terephthalate units which provide denser packing, as well as the presence of several glycols which also give improved physico-mechanical properties [10]. The results obtained from the studies provoked a number of new ideas and new possibilities for improvement of the physico-mechanical properties which would widen the application range of this type of unsaturated polyesters.

#### Conclusion

The results showed that waste PET and crude glycerol can successfully be used for preparation of unsaturated polyester resins. Under certain temperature regime and in absence of catalysts, glycolysis of PET with crude glycerol was carried out to obtain linear polyester polyols. The latter were separated using their water solubility difference at 4°C and 90°C. WSF and WIF were then used as initial product for synthesis of UPE where 34-36 wt% of the necessary initial monomers were replaced. Unsaturated polyester resins were then prepared and solidified. After curing, barcol hardness, flexural and tensile strength were investigated. The present work is of certain scientific, practical and ecological importance.

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