

# Post-consumer PET Bottles Recycling

## III. Obtaining of unsaturated polyester resins and mechanical characterization of cross-linked materials with styrene

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*Poly(ethylene terephthalate) PET was subject to a glycolysis process using diethylene glycol (PET/DEG = 1/1 molar ratio) and zinc acetate as trans-esterification catalyst. An unsaturated polyester resin was then prepared using the glycolysis product and maleic anhydride. The molecular weights of glycolysed PET products and polyester resin were investigated using gel permeation chromatography (GPC) analysis. A cross-linking reaction of the unsaturated polyester resin was performed in the presence of styrene (different amounts) at 80°C. The compression and impact strength/resistance properties of the cured resins were determined.*

*Keywords: PET waste, glycolysis, GPC, unsaturated polyester resin, mechanical properties*

In the last 20 years, the world has become aware of the concept of environmental protection and recycling in terms of non-renewable resources. More stringent legislative regulations regarding environmental conditions are imposed motivating the development of innovative technology based on recycling as well as establishing a strict waste management control. In Japan, since May 2000, 'The Basic Law for Establishing the Recycling-based Society' ensures the legal conditions for the proper reuse of materials, recycling and waste disposal, based on the idea that all plastics will ultimately be required to be recycled [1].

In Europe, effective actions have been taken in order to reduce the amount of packaging waste with 70% by the year 2006 [2]. The United States is one of the largest user of poly(ethylene terephthalate) (PET) packaging [3], while Brazil and Latin America generally showed the fastest growing consumer markets for PET bottles between 2001 and 2006 [2].

In Romania, the management of packaging and packaging waste is in accordance with European's Union legislation based on Directive No. 2008/98/CE and the general principles set forth in E.O. No. 78/2000 on waste regime. The principles of waste management of packaging refer to: (1) prevention of packaging waste, (2) reuse of packaging, (3) recycling of packaging waste, and (4) other forms of recovery for packaging waste.

Considering these principles, various technologies have been developed to recover suitable substances from PET for chemical industries involving mechanical, and energy recovery or chemical reconversion.

The mechanical methods are based on the sorting and separations of the wastes, size reduction, melt filtration and reforming of the plastic material. The major drawback of this type of recycling consists in the deterioration of product properties in every cycle [4, 5].

The energy content of the plastics waste can be recovered by incineration when the sorting and separation of plastics waste are difficult. Although this method was

considered to be economically viable, it has been widely accused of being ecologically unacceptable based on the health risk from air that can be contaminated with toxic substances in some cases [4, 5].

For these reasons, the degradation process of PET was intensively investigated using chemical recycling starting from various reagents such as water (hydrolysis), alcohols (alcoholysis), acids (acidolysis), glycols (glycolysis), and amines (aminolysis) [6-11]. Using a different reagent for the depolymerization reaction, different products can be obtained.

In this paper, the degradation products from PET waste were obtained using a glycolysis procedure. Generally, the glycolysis reaction represents the degradation of PET polymer by glycols (ethylene glycol [12], diethylene glycol [13], propylene glycol [14]), in the presence of trans-esterification catalysts, mainly metal salts [15].

The utilization of glycolysed PET products have found applications in unsaturated polyester resins [16], polyurethane foams [17], additives for concrete [18], organic coatings [19], adhesives [20].

The aim of this study consisted in the synthesis of an unsaturated polyester resin starting from chemical recycling of PET waste using diethylene glycol. The unsaturated polyester resin was obtained by a polycondensation reaction of the glycolysed PET with maleic anhydride. The double bonds from the polyester chain were cross-linked in order to obtain a cross-linked polyester molding compound with possible applications in construction field for panels, floors or partition walls.

### Experimental part

#### Materials and methods

PET flakes with rectangular shape, with a diagonal of around 10-12 mm, obtained by industrial recovering of post-consumer PET bottles, were used as received. The intrinsic viscosity in 60:40 (w/w) phenol - 1,1,2,2 tetrachlorethane solution at 25°C, is about 0.65 dL/g corresponding to a number-average molecular weight of approximately  $3 \cdot 10^4$  g/mol. Diethylene glycol (DEG) (Merck) was purified by

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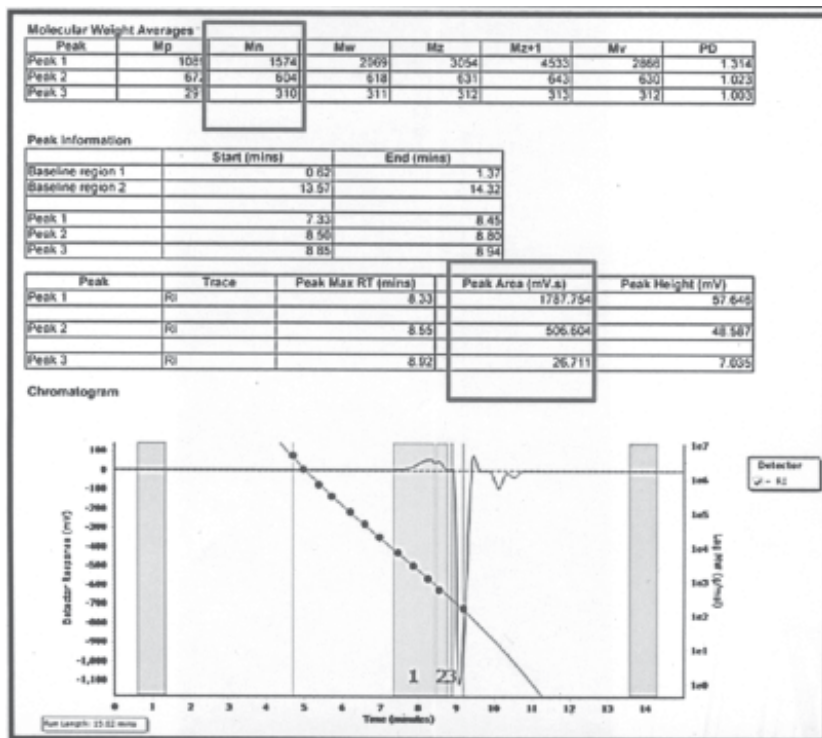


Fig. 1. Molecular weights of resulted oligomers and their concentration

vacuum distillation at 148°C/20 mmHg. Styrene (ST) (Aldrich) was purified by vacuum distillation at 60°C and 40 mmHg. Zinc acetate ( $Zn(CH_3COO)_2$ ) (Aldrich), maleic anhydride (Aldrich), toluene (Merck) were used as received. Lauroyl peroxide (PL) (Aldrich) was purified by recrystallization from ethanol.

#### Depolymerization reaction of PET

The glycolysis reactions were carried out following a procedure used in our previous study [21]. PET flakes and DEG have been added in a four-necked round bottom reactor mechanically stirred, fitted with a condenser, a thermometer and a nitrogen inlet. The stirring was set to 200-300 rot/min. At the start of the reaction the amount of DEG seems insufficient to ensure a proper agitation, but this is quickly overcome as the temperature increases and the PET flakes are dissolved in DEG (about 0.5 h). The reaction is first heterogeneous, then homogeneous and continuously the viscosity of the system decreases as the glycolysis reaction proceeds. The experiments were carried out at 220°C for 5 hours and involved a molar ratio of PET/DEG = 1/1.  $Zn(CH_3COO)_2$  was used as a trans-esterification catalyst (0.5% by weight of PET).

#### Polyesterification reaction

The polyesterification reaction was carried out in the presence of a certain amount of depolymerized PET and a corresponding amount of maleic anhydride. The temperatures regime was strictly observed: 100°C for 1 h; 150°C for 2 h and the addition of 30 mL of toluene that allowed the removal of the resulting water from the reaction mixture using a Dean-Stark apparatus; 200°C for 2 h.

#### Cross-linking reactions

The obtained unsaturated polyester was solubilized in ST (different amounts) and cross-linked with PL at 80°C for 4 h.

#### Characterization

The molecular weights of the resulted oligomers and polyester were analyzed using *PL-GPC 50 Integrated GPC/SEC System (Agilent Technologies)*.

The mechanical properties of the obtained cross-linked materials were measured on an *Instron 3382 instrument*, equipped with a 100 kN cell at room temperature ( $23 \pm 1$  °C) and  $50 \pm 10\%$  relative humidity. The cylinder-shaped samples (10 mm diameter, 10 mm height  $\pm 0.2$  mm) were placed on the lower plate and compressed by the upper plate at a constant compression rate of 2 mm/min until a relative deformation of 90% was attained, without breaking of the samples.

Impact resistance tests were performed on the samples which were milled to make standard Izod V notch specimens as per SR EN ISO 180:2001 standard using a specialized Tinus Olsen drill milling machine. The impact tests were realized using a Tinus Olsen IT 504 pendulum.

#### Results and discussions

##### Conventional depolymerization reaction of PET

Previous results [21] revealed that the most promising specimen to obtain unsaturated polyester originates from PET and DEG in a weight ratio of 2:1 (1/1 molar ratio). The depolymerization reaction was carried out at 220°C for 5 h using  $Zn(CH_3COO)_2$  as catalyst.

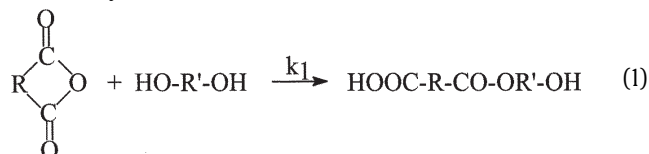
The hydroxyl index is a very important parameter for the subsequent reaction of polycondensation with maleic anhydride. For this reason, after the degradation process, the resulted oligomers mixture has been characterized by GPC analysis in order to establish their concentration and molecular weights (fig. 1).

Figure 1 presents clear evidence that there are three species with different molecular weights: 1574 g/mol, 604 g/mol and 310 g/mol. The concentration of these specimens is represented by a different peak area. Knowing the molecular weights and their corresponding concentration, the hydroxyl index can be calculated in order to determine the necessary amount of maleic anhydride for the polycondensation reaction. In our case, 140 g of glycolyzed PET resulting from the depolymerization reaction were reacted with 13 g of maleic anhydride.

### Polycondensation reaction

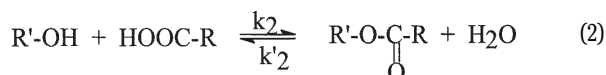
Unsaturated polyesters represent the products of polyesterification reaction of polycarboxylic acids (or their corresponding anhydrides) with polyhydric alcohols. The unsaturated nature given to the final product is based on the presence of an unsaturated polycarboxylic acid or its corresponding anhydride in the initial monomer mixture. Without exception, the applications of unsaturated polyesters involve the consumption of vinyl groups using radical cross-linking copolymerization with various vinyl monomers.

Polyesterification processes/reactions based on anhydrides of dicarboxylic acids involve a sequence of two elementary reactions characterized by different kinetic and thermodynamic mechanisms:



-to simplify –R– was found not to influence the formation rate of hydroxyl carbonylestere.

- the resulting carboxyl groups further react with the hydroxyl groups affording the final polyesters;



The addition reaction (1) is fast, spontaneous, equilibrium shifted to right and exothermic. Consequently, this reaction takes place mainly in the first part of the process.

The esterification reaction (2) is slow, has the character of equilibrium ( $K = \frac{k_2}{k_2'} < 10$ ), the shifting of the balance is realized by the removal of the by-product (water) and is overall endothermic, especially due to the amount of heat required to evaporate water from the system.

Usually, the polyesterification reaction follows a temperature program as presented previously. Reaction (1), with the above mentioned characteristics is responsible for a susceptible polyesterification reaction based on the hydroxylic and carboxylic compounds. If the functional groups are not balanced, the reaction will stop by itself when minority group is consumed.

For mixtures of difunctional compounds with  $N_{\text{COOH}} \neq N_{\text{OH}}$ , process and product characteristics can be expressed as follows:

$$\bar{p} = 2x / (N_{0,\text{COOH}} + N_{0,\text{OH}}) \quad (1)$$

$$p_{\text{COOH}} = x / N_{0,\text{COOH}}; \quad p_{\text{OH}} = x / N_{0,\text{OH}} \quad (2)$$

$$x = N_{0,\text{COOH}} - N_{0,\text{OH}} \quad (3)$$

$$\overline{\text{GP}}_n = 1 / (1 - \bar{p}) \quad (4)$$

where:

$\bar{p}$  = extent of polyesterification ;

$x$  = number of functional groups –COOH (or –OH) that have reacted;

$N_{0,\text{COOH}}$ ;  $N_{0,\text{OH}}$  = number of functional groups –COOH, respectively –OH initially present;

$p_{\text{COOH}}$ ;  $p_{\text{OH}}$  = extent of reaction for functional group (–COOH, or –OH);

$\overline{\text{GP}}_n$  = number average degree of polymerization.

The correlation of equations 1-4 with experimental data:

$$\bar{p} = 2x / (N_{0,\text{COOH}} + N_{0,\text{OH}}) = 2V_{\text{H}_2\text{O}} / [V_{\text{H}_2\text{O}}^t (1 + r)] \quad (1')$$

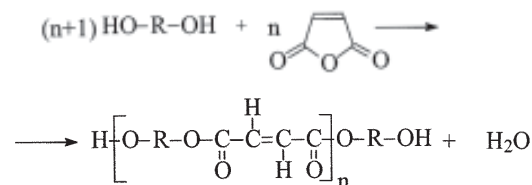
$$p_{\text{COOH}} = V_{\text{H}_2\text{O}} / V_{\text{H}_2\text{O}}^t; \quad p_{\text{OH}} = V_{\text{H}_2\text{O}} / r \times V_{\text{H}_2\text{O}}^t \quad (2')$$

where:  $r = N_{0,\text{OH}} / N_{0,\text{COOH}}$ ;

$V_{\text{H}_2\text{O}}^t$  = theoretical volume of disposed water when minority functional groups are consumed (mL);

$V_{\text{H}_2\text{O}}$  = experimental volume of disposed water (mL).

Overall, the global reaction is:



Knowing the number of functional groups initially present, respectively the theoretical value of the disposed water, it is easy to calculate the extent of the reaction by measuring the water volume discharged. The calculated values are presented in figure 2.

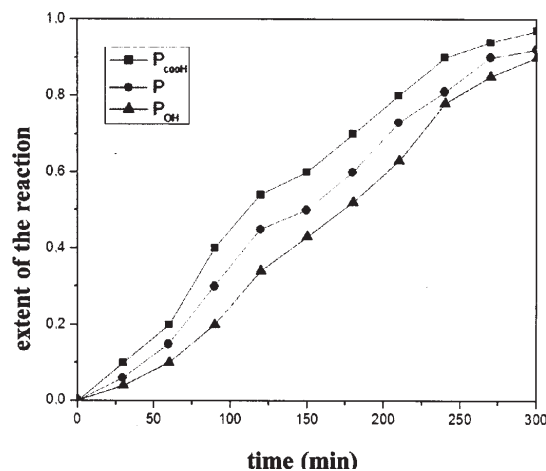


Fig. 2. The evolution in time of reaction extent

The value of the extents for –OH groups is smaller than for –COOH groups due to the fact that –COOH functional groups are in minority. In conclusion, the macromolecular chains will present –OH end-groups.

### Testing the reactivity of unsaturated polyester – cross-linking

The GPC analysis afforded the results for the molecular weight of the obtained polyester (fig. 3) in order to establish the number of double bonds –CH=CH– from the main chain. This information proved to be essentially for the cross-linking reaction.

The mixture provided from polycondensation is composed by two components with different molecular weights. Thus, the molecular weight of the unsaturated polyester resin (UPR) is 2876 g/mol and is the majority product of the reaction.

The cross-linking of the UPR was performed using ST at different weight ratios (UPR/ST: 1/1, 1/1.5, respectively 1/2) at 80°C for 4 h, using PL as initiator. The obtained materials were subsequently subject to compressive and impact resistance mechanical tests using standardized methods. The values of compressive stress (MPa) and Young's modulus (MPa) are given in table 1 for each specimen.

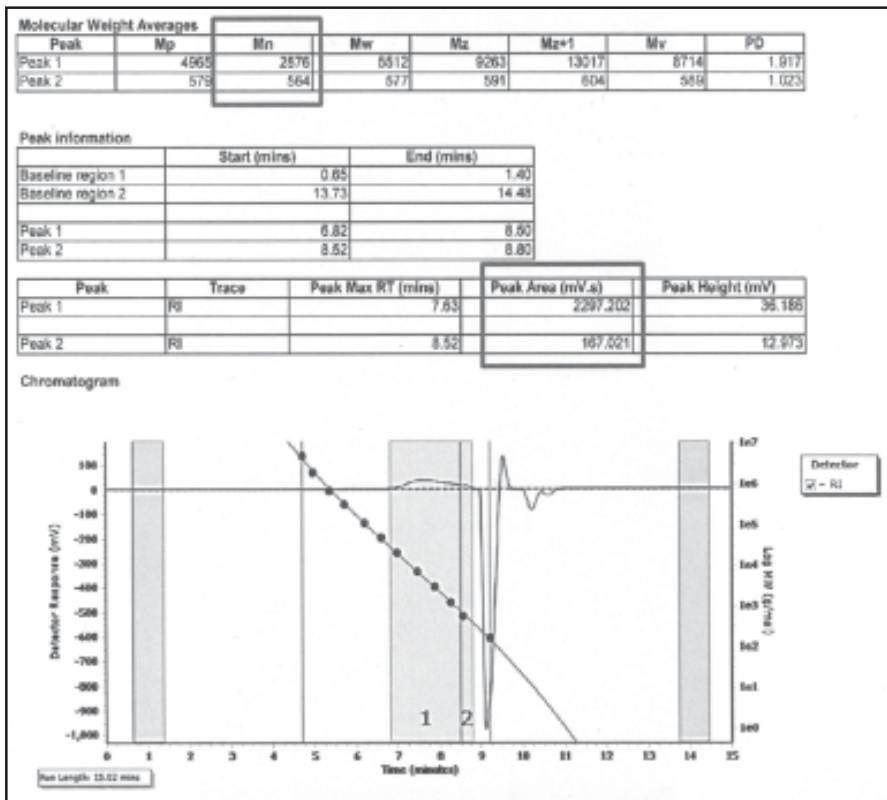
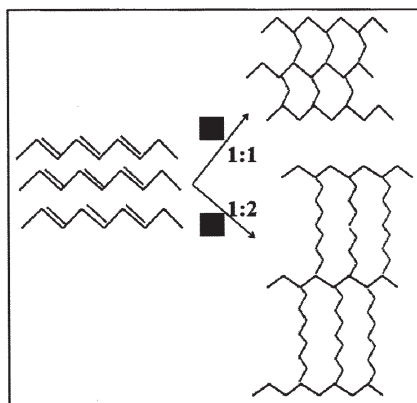


Fig. 3. GPC analysis for the obtained unsaturated polyester resin

The values of Young's modulus decrease as the amount of **ST** increases. This aspect can be explained by the homopolymerization reaction of **ST** that has a higher occurring rate than the **copolymerization** reaction [22]. For this reason, it is expected that polystyrene chains are incorporated in a cross-linked network of **UPR**, leading to a decrease in Young's modulus (scheme 1).



Scheme 1. Cross-linking of polyester unsaturated chains using different ratios UPR/ST

Moreover, the compressive stress has higher values for the specimens with lower concentration of **ST**, leading to the formation of denser cross-linked networks.

The compressive stress-strain curves (fig. 4) complements the results presented in table 1, showing that the **UPR/ST 1-1** specimen registered the highest compressive stress (120 MPa) at 6-7%.

The Izod impact resistance tests results are presented in table 2. The resistance values confirm the compression tests results, the highest impact resistance being registered for the samples with a **UPR/ST** ratio of **1/1**. These values can be also explained by a denser cross-linked network.

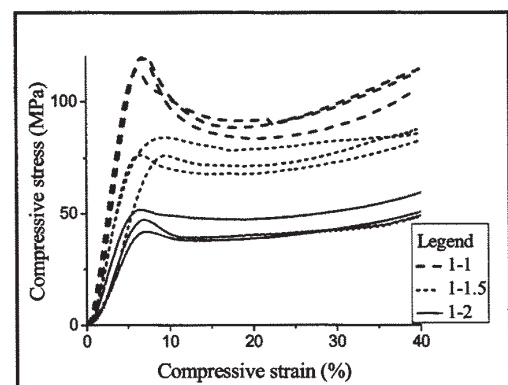


Fig. 4. Compressive stress-strain curves for different ratios between the UPR and ST (1-1, 1-1.5 and 1-2 (w/w))

Table 1  
COMPRESSION MECHANICAL TEST RESULTS

No.	Compressive stress at yield (zero slope) (MPa)	Young's Modulus (MPa)
Ratio 1-1		
A	120.83	2717.73
B	119.94	2675.90
C	114.39	2628.47
Ratio 1-1.5		
A	76.07	1353.13
B	84.00	1795.77
C	76.30	1876.86
Ratio 1-2		
A	51.56	1254.61
B	41.54	928.80
C	47.05	1139.90

**Table 2**  
IZOD IMPACT RESISTANCE TESTS RESULTS

IZOD	Resistance (kJ/m <sup>2</sup> )	Average resistance (kJ/m <sup>2</sup> )
Ratio 1-1		
A	2.0728	2.1165
B	2.12385	
C	2.1529	
Ratio 1-1.5		
A	2.01035	2.0174
B	2.05869	
C	1.98312	
Ratio 1-2		
A	1.98108	1.9773
B	1.93855	
C	2.01228	

### Conclusions

The aim of this study consisted in the synthesis of an unsaturated polyester resin starting from chemical recycling of PET waste using DEG in a molar ratio 1:1. The unsaturated polyester resin was obtained by a polycondensation reaction of the glycolized PET with maleic anhydride. The double bonds from the polyester chain were cross-linked with ST in order to obtain a cross-linked polyester molding compound with possible applications in construction field for panels, floors or partition walls. The values of Young's modulus and the compressive stress have higher values for the specimens with lower concentration of ST, leading to the formation of denser cross-linked networks. This aspect is also confirmed by the increased impact resistance which is higher at lower concentration of ST.

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