Unsaturated polyester resins based on waste products with low styrene emission

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Abstract
Glycolysis of polyethylene terephthalate was carried out with crude glycerol. Three fractions were separated from the product obtained on the basis of their solubility in water. Three kinds of unsaturated polyesters were synthesized by polycondensation of each fraction with propylene glycol and maleic anhydride.

To prepare unsaturated polyester resins, usually styrene is added to unsaturated polyesters. In the present work, unsaturated polyester resins of low styrene emission were obtained by substituting part of styrene with methyl methacrylate. The solidification was carried out using cobalt naphthenate and methylethyl ketone peroxide as accelerator and initiator, respectively. Some basic physicomechanical properties of the solidified systems were studied.

Keywords: Recycling, polyethylene terephthalate, crude glycerol, unsaturated polyesters

1. Introduction
Glycolyzates of waste polyethylene terephthalate (PET) find application in the manufacture of unsaturated polyester resins (UPER). Various glycols are used for PET depolymerization – ethylene glycol, propylene glycol (PG), diethylene glycol and their mixtures (Duque-Ingunza et al., 2013, Waigaonkar et al., 2011) [2, 6]. The literary data on PET depolymerization with crude glycerol (CGly) followed by synthesis of UPER are scarce. This possibility was discussed in our earlier publication (Todorov, 2016) [4].

The technology for synthesis of UPER involves three stages: synthesis of unsaturated polyesters (UPE), preparation of UPER and solidification of UPER. Usually, Styrene (St) is used during the solidification of the UPE (Osman. et al., 2012. Cao and Lee, 2003, Todorov, 2015) [1, 3, 5]. It is a good solvent and crosslinking agent but its emission in the environment poses risks to human health.

The present work is a continuation of our previous experiments and its aim is to study the influence of the different length of the depolymerized chains on the process of polyesterification and the properties of the UPER. To reduce the impact on the environment, the possibility to obtain unsaturated polyester resins with low styrene emission was also studied.

2. The objectives of the study
2.1 Materials
PET flakes were obtained from beverage bottles. CGly was purchased on the market. PG, toluene and maleic anhydride (MA) were of grade pure for analysis. KOH, toluene, St, methyl methacrylat(MMA), Pb acetate, 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, 22.5g CGly (0.2 mol Gly) and 2.3 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 19.2 g (0.1 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 180 min.
2.3 Fractionation
To fully separate the polyester precursor monomers, the reactor content was cooled to room temperature and a total of 1000 ml cold distilled water was added three times. The mixtures were vigorously agitated followed by filtration. The filtrates obtained were concentrated to a volume of 300 ml by heating to boiling temperature. The concentrated filtrate was kept in refrigerator at 4 °C for 8 h. The white residue obtained was again filtered, purified and dried at 60 °C. It was denoted as fraction (A).

To the product of the depolymerisation, which had not been dissolved in cold water, 200 ml distilled water were added, and the mixture was boiled under vigorous agitation. It was hot-filtered and the filtrate was immersed in ice bath, to obtain white precipitate. The latter was then filtered, purified and dried at 60 °C. It was denoted as fraction (B).

The product which was not dissolved in hot water was washed several times with hot distilled water and dried at 60 °C. It was denoted as fraction (C).

2.4 Preparation and solidification of unsaturated polyester resins
In a round bottomed flask of 250 ml equipped with mechanical stirrer, Dean-Stark apparatus, thermometer and inert gas inlet, 14.8 g (0.04mol) from fraction A, 10 g (0.131mol) PG, 15.2 g (0.155mol) maleic anhydride and 4.2 g toluene are placed. The polyesterification begins at 130 °С. The temperature was gradually raised to 200 °С. The process kinetics was monitored by measuring the acid number.

With the same experimental equipment, the polyesters obtained were cooled to 70 °С and 10.4 g styrene were added. After full homogenization, 8 g MMA were added followed by homogenization. To initiate the solidification, 2 wt.% CoNp as accelerator and 1% MEKP as initiator were added. The process was carried out temperature of 35 °С for 12 h.

By the same technique, the unsaturated polyester resins were obtained in the composition of which fraction B or C was included.

2.5 Analysis and characterization
- **Acid number**: Determined according to EN 14104:2003.
- **Analysis of Cgly**: The contents of glycerol, water and ashes were determined according to the standards EN 14106:2003, ISO 12937:2003 and ISO 3987:1999, respectively.
- **FT IR spectroscopy**: The IR spectrum of glycolysed product was analyzed from a thin film of sample on a KBr cell using a Nicolet iS 50 FT.
- **Indentation hardness**: Was measured with GYZJ 934-1 Barcol impressor according to ASTM D 2583-99.

3. Results And Discussion
For the preparation and solidification of UPERs, four stages were completed in the experiments reported: glycolysis of waste PET with Cgly, polyesterification, mixing the obtained unsaturated polyesters with St and MMA and solidification. The process can be illustrated by Scheme 1.

The composition of the Cgly was determined by standard methods. The glycerol content was found to be 80,5%, water – 10,8 and ashes – 6,3%. The content of matter organic non-glycerol (MONG) was calculated from the difference: (100 - (% glycerol content + % water content + % ashes content).

The glycolysis was carried out at molar ratio Cgly/PET=2. By a technique described above, three fractions were separated – A, B and C. It has been found that the number average molecular mass is 350, 750 and 1200 for the fractions A, B and C, respectively.

It is important to note that the glycolysis product had dark brown color while the separated fraction A and B were white and fraction C – light brown. Therefore, the fractionation separates the depolymerized products from the impurities present in the crude glycerol.

Each of the fractions A, B and C was used as precursor for the preparation of unsaturated polyesters -UPE-1 UPE-2 UPE-3 соответственно.

The amount of MA was calculated so as the ratio hydroxyl/carboxyl groups to be 1, 1. The kinetics of the process was monitored by measuring the acid number (Fig.1).

Despite that the shapes of the curves are almost identical, substantial differences in the change of the acid number can be observed. The acid number of UPE-1 changed at the highest rate while for upe-2 and UPE-3 the change was more gradual. Values of the AN≤50 were reached almost simultaneously.
To prepare unsaturated polyester resins, solvent was added to the unsaturated polyesters which also played the role of a crosslinking agent. The most often used one in the technology of UPER synthesis is St. The disadvantage here is in the high level of styrene emissions both during the dissolution and the solidification.

In the present work, aiming to obtain unsaturated polyester resins with low styrene emission, part of St was substituted by MMA. A total of 6 kinds of UPER were synthesized /Table 1/. For the solidification of each one of them, 2 wt% CoNp was used as accelerator and 1% MEKP as initiator. The substitution of part of the St with MMA resulted in substantially lower styrene emissions during the dissolution. The reduction of styrene emissions was observed also after the solidification. The content of residual styrene in the solidified products was studied by the method of IR spectroscopy. Free styrene has two absorption bands in the interval 900-1000 cm⁻¹. They can be seen at 912 cm⁻¹ and 992 cm⁻¹ and are attributed to the out-of-plane vibrations of the C–H bond in the vinyl groups CH=CH₂. These bands can be used for quantitative determination of the free St despite the overlapping with the band at 982 cm⁻¹ attributed to the out-of-plane vibration of the C–H bond in the group CH=CH of the fumaric units in UPEs. To eliminate the changes which might occur due to changes in the film thickness or transparency, the band at 2940 cm⁻¹ attributed to the valent vibrations of the CH₂ groups was used as internal standard. The quantitative determination /Table 1/ was made by the method of the calibration curves.

It can be seen that the residual styrene present in the samples where part of St was replaced by MMA decreased up to 20 times during the solidification. This can be explained with the styrene affinity to copolymerization with MMA. It has been reported (Cao and Lee, 2003) [1] that the rate of the styrene homopolymerization reaction in significantly lower than that of its copolymerization with MMA.

Product transparency is important in many cases. By solidification in presence of 20 wt% styrene and 15 wt% MMA, the samples become transparent. Among tensile properties, the hardness by Barcol was measured. Two conclusions can be made from the results obtained (Table 1). The first one is that the hardness of the solidified products increases with the substitution of part of styrene with MMA and the second one – hardness depends on the length of the precursory depolymerized products - the lower the molecular weight, the higher the hardness corresponds. This can be explained with the more uniform distribution of the double bonds in the UPER which facilitates the formation of more uniform spatial network during the solidification.

### Table 1: Some basic characteristics of solidified unsaturated polyester resins

<table>
<thead>
<tr>
<th>UPE kind</th>
<th>Styrene, % per 100g UPE</th>
<th>MMA, % per 100g UPE</th>
<th>Transparency</th>
<th>Content of residual Styrene, %</th>
<th>Barcol hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>UPE-1</td>
<td>35</td>
<td></td>
<td>opaque</td>
<td>35</td>
<td>8,3</td>
</tr>
<tr>
<td>UPE-1</td>
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<td>15</td>
<td>transparent</td>
<td>0,3</td>
<td>53</td>
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<td>UPE-2</td>
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<td>15</td>
<td>opaque</td>
<td>9,1</td>
<td>47</td>
</tr>
<tr>
<td>UPE-3</td>
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<td></td>
<td>transparent</td>
<td>0,4</td>
<td>51</td>
</tr>
<tr>
<td>UPE-3</td>
<td>20</td>
<td>15</td>
<td>opaque</td>
<td>11,2</td>
<td>45</td>
</tr>
</tbody>
</table>

5. References