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# Surface coatings based on glycerol phase and waste polyethylene terephthalate

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The aim of this paper is to investigate the possibility for using two waste products - glycerol phase derived from biodiesel production and waste poly(ethylene terephthalate) (PET) from non-alcoholic beverage bottles for preparation of surface coatings. Four medium oil alkyds were prepared - two from organic substances, contained in glycerol phase, different amounts of PET and phthalic anhydride, the other two were for reference and were synthesized from glycerol, sunflower oil, ethylene glycol and phthalic anhydride. Structure of all alkyds was confirmed by FTIR and $^1$H NMR spectroscopies.

From all alkyds surface coatings on glass plates were obtained. Their physical properties (drying degree, hardness, adhesion) and chemical resistance were investigated. The analysis showed that the alkyd resins based on the organic substances in glycerol phase, PET and phthalic anhydride are superior to reference alkyds in terms of drying degree and hardness.

**Keywords**: coatings, biopolymers, glycerol phase, alkyd resins.

## INTRODUCTION

Surface coating is a solid or liquid material in combination with pigments and solvents, that is spread over a surface to form a thin film. This film can protect the surface from the elements or has a decorative function, or both. Therefore, surface coatings are widely used in most industries.

Alkyd surface coatings are the most consumed coatings used worldwide, despite the increasing use of other film formers. Alkyd resins are a special family of polyesters synthesized by condensation reaction of oils or fatty acids, dibasic acids or acid anhydrides and polyols with hydroxyl functionality greater than two. The traditional oils such as linseed oil, sunflower oil, soybean oil and safflower oil are used for their synthesis [1-3].

Sunflower oil has an iodine value of 110-140 g $I_2$/100 g and is accentuated to semi-drying oils. The advantages of semi-drying oils are that after curing their surface is smooth, stays clear, which makes them good for coloring.

Sunflower oil is the second most used feedstock for biodiesel production after rapeseed oil in Europe [4]. Biodiesel production generates glycerol phase (GPh) as a main byproduct. The excess GPh may become an environmental problem since it cannot be disposed to the environment [5]. Its utilization is difficult due to its complex and variable composition. It contains glycerol, water, methanol, soaps, fatty acid methyl esters (FAMEs) biodiesel, free fatty acids (FFAs), mono-, di- and triglycerides. There have been many investigations considering the utilization of the glycerol from the glycerol phase [6, 7].

Information in literature about the use of other organic substances besides glycerol in the glycerol phase is scarce. Their quantity is ~30% [8] and utilization is of ecological and economic significance. Among the possibilities, much attention is drawn to the polymer chemistry and technology [9].

Besides utilization of the glycerol phase, for the present work it was also important to utilize waste poly(ethylene terephthalate) (PET). The increasing worldwide usage of PET, along with economic and ecological pressures, have caused the waste polymer recycling technologies to be in the scope of interest for many scientists [10].

Waste PET from non-alcoholic beverage bottles can be used in preparation of surface coatings [11-14].

Considering this background, the following goals of the current study were formulated - to use all organic substances in the glycerol phase and waste PET for synthesis of alkyds, and to expand the knowledge on composition and properties of the obtained alkyd resins.

## EXPERIMENTAL

### *Materials*

Glycerol phase (GPh-1S) was obtained from Biogaz Inzhenering SD, Burgas, Bulgaria. Sunflower oil (SFO) was purchased on the market. Waste PET from non-alcoholic beverage bottles, chopped into flakes with size 0.8 – 1.2 mm, was used. Glycerol (Gly), ethylene glycol (EG), potassium hydroxide (KOH), phthalic anhydride (PhA), methanol, potassium hydroxide, xylene,

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Pb acetate and Co naphthenate were purchased from Aldrich and used without further purification.

### *Analytical methods*

Basic characteristics of GPh-1S, crude glycerol (CGly-1S) and sunflower oil fatty acid (SOFA) were determined. Glycerol content and methanol content were determined by high performance liquid chromatography (HPLC-1200), pH - by pH meter (Metrohm, 827 pH Lab). According to standardized methods of analysis were determined water content [15], ash content [16], organic non glycerol (MONG) content [17], Gardner color [18], FFAs content [19], iodine value [20], acid value (AV) [21] and density [22].

### *Synthesis of alkyds Alk-1S12 and Alk-1S20*

Calculated amount of CGly-1S, toluene as azeotropic solvent and a portion of SOFA-1S (to which 0.2% KOH was added) were charged into a round bottomed flask, equipped with mechanical stirrer, thermometer, inert gas inlet and Dean-Stark separator. Temperature at the beginning was 85°C until the water from CGly-1S was completely evaporated. The temperature was then raised to 200°C. The process of esterification was monitored by acid value determination every 15 min and conversion of SOFA-1S was calculated by the equation:

$$Conversion, \% = \frac{A_o - A_t}{A_o} . 100 \qquad \text{Eq. 1}$$

where: $A_0$ is the initial acidity of the mixture; $A_t$ acidity at any time t.

The process of esterification is considered to be accomplished, when conversion is ~100%.

The temperature was then raised to 220°C and a preliminarily calculated amount of PET flakes heated to 220°C was added to the reaction system. A heterogeneous mixture of solid PET flakes and liquid product of the esterification was formed. Interaction continued until full homogenization of the mixture. The temperature was then lowered to 170°C and calculated amounts of phthalic anhydride and toluene were added. When viscosity of the system started increasing, the temperature was gradually raised to 240°C and stirring was intensified.

The reaction was monitored by acid value determination every 30 min. The polyesterification reaction was carried out until 10 mg KOH/g was obtained.

### *Preparation of films from alkyd resins and testing*

All alkyds after esterification process with phthalic anhydride were cooled to 70°C and a calculated amount of xylene was added to obtain 60% solutions (alkyd resins). Then only for alkyd resins AR-1S12 and AR-1S20 hot filtration was carried out for separation of potassium phosphate, which is the last contaminant in alkyd resins resulting from the use of CGly-1S and SOFA-1S. To accelerate drying of all alkyd resins, 1% of Pb and 0.1% of Co were added. Using a 50 μm applicator, the prepared solutions were applied on glass plates. Films were air-dried at 25°C for 24 h and then were heated to 110°C for 2 h.

The physical properties and chemical resistance of the films were investigated according to standardized methods [23-26]. Drying degree was determined by Erichsen 415 apparatus. Hardness was determined by Elcometer 501 Pencil hardness tester. Adhesion strength was measured by Elcometer 107 Cross Hatch Cutter tester.

### *Instrumental methods of analysis*

FTIR **s**pectra were recorded with Bruker Tensor 27 within the interval 4000 to 400 $cm^{-1}$ with resolution of 2 $cm^{-1}$. Samples were prepared as thin film fixed between two discs of KBr to avoid the presence of air.

$^1$H NMR spectra were recorded on a Bruker Avance II+ 600 (600.13 for $^1$H NMR and 150.92 MHz for $^{13}$C NMR) spectrometer with TMS as internal standard for chemical shifts (δ, ppm).

## RESULTS AND DISCUSSION

### *Treatment of glycerol phase GPh-1S*

The composition of GPh-1S was determined (Table 1). The content of non-glycerol organic matter (MONG) was 28.8% by weight of the glycerol phase and 66% by weight of the glycerol.

**Table 1.** Composition of GPh - 1S

| Glycerol phase GPh – 1S | |
|---|---|
| Content, wt.% | Value |
| Glycerol | 47.4 |
| Methanol | 7.8 |
| Water | 13.8 |
| MONG | 28.8 |
| Ash | 2.2 |

All organic substances (glycerol and MONG) can be successfully used after employing two easy chemical processes. The first one is saponification. It is carried out with alcoholic solution of KOH until pH reached 11. FAMEs and the glycerides are converted to soaps.

The second process is acidification with phosphoric acid. This process transforms soaps into free fatty acids while KOH reacts to give potassium phosphate.

**Table 2.** Basic characteristics of the CGly-1S and SOFA-1S

| CGly-1S | | SOFA-1S | |
|---|---|---|---|
| Glycerol content, wt.% | 82.3 | FFAs content, wt.% | 98.2 |
| Density at 20°C, g/cm$^3$ | 1.23 | Density at 20°C, g/cm$^3$ | 0.918 |
| Water content, wt.% | 12.9 | Saponification value (mg KOH/g) | 190 |
| MONG content, wt.% | 2.5 | Iodine number, gI$_2$/100g oil | 126.6 |
| Ash content, wt.% | 2.3 | Average molecular weight (g/mol) | 280 |
| Gardner color | 6 | Gardner color | 8 |

As a result, a solid phase of salts (potassium phosphate) in the liquid phase was formed. Potassium phosphate is the main contaminant in the reaction mixture. It was separated from the fluid after settling for about 1 h. Without special purification it can be used as fertilizer and as buffer solution.

The obtained liquid phase contained glycerol and SOFA-1S. They are mutually insoluble and quite different by density. If stored overnight, they form layers. The light one SOFA-1S contains mainly free fatty acids (FFAs) and the heavy layer contains mainly glycerol. Subsequently the lower layer was neutralized with 12.5 M KOH until the pH was 7. As a result, the crude glycerol CGly-1S was obtained. Some basic characteristics of SOFA-1S and CGly-1S, obtained from glycerol phase were determined (Table 2).

The obtained SOFA-1S contains 98.2 wt.% higher fatty acids. The other 1.8 % is glycerol. The color of fatty acids (Gardner color = 6) is darker than the typical for fatty acids color of sunflower oil (Gardner color = 4), which may be due to the production process. Complete removal of MONG, water and potassium phosphate from CGly-1S was not achieved.

### *Theoretical calculation of alkyds compositions*

Four medium oil alkyds were formulated for the purpose of this work. CGly-1S, SOFA-1S, different amounts of PET waste and phthalic anhydride were used for synthesis of Alk-1S12 and Alk-1S20. Glycerol, sunflower oil, ethylene glycol and phthalic anhydride were the raw materials for Alk-RS12 and Alk-RS20.

To avoid gelation, all alkyds were formulated according to Patton’s gel point calculation. Alkyds were formulated to have oil length of 50% (Table 3).

Values of the Patton’s gel point constant K were from K = 1.07 to K = 1.08 which means that no gelation will occur at 100% reaction accomplishment.

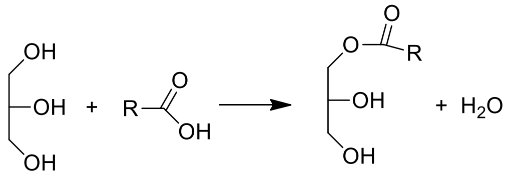
### *Preparation of alkyds Alk-1S12 and Alk-1S20*

Alkyds Alk-1S12 and Alk-1S20 were synthesized by a three - stage process.

**Table 3**. Composition of alkyd resins

| | Alk-1S12 | Alk-1S20 | Alk-RS12 | Alk-RS20 |
|---|---|---|---|---|
| SFO | - | - | 52.3 | 52.3 |
| SOFA | 50.0 | 50.0 | 50.0 | 50.0 |
| PhA | 28.0 | 23.0 | 37.8 | 37.8 |
| PET | 12.0 | 20.0 | | - |
| EG | - | - | 3.9 | 6.5 |
| Gly | - | - | 21.3 | 18.7 |
| CGly: | 25.8 | 22.0 | - | - |
| Gly | 21.2 | 18.1 | - | - |
| MONG | 0.4 | 0.4 | - | - |

During the first stage, monoglycerides from SOFA-1S and CGly-1S were obtained. The main reaction is the interaction of the SOFA-1S carboxyl groups with the primary OH groups of glycerol (Scheme 1):



**Scheme 1.** Esterification of glycerol with fatty acids

Along with the main reaction, side reactions may occur. It is known [11] that diglycerides are always formed simultaneously with monoglycerides. Side reactions may also occur because of impurities in the reaction system. In MONG composition there are FAMEs. Under the reaction conditions, glycerolysis of FAMEs may occur and monoglycerides can be obtained.

The esterification process was estimated by the changes in the acid value. Then conversion was calculated according to formula 1. The process of esterification was considered to be accomplished when conversion was ~100 % (Fig. 1).

Conversion of the carboxyl groups into the esters was confirmed by FTIR spectroscopy. For fatty acids, stretch vibrations of the C=O bonds appear at 1714 cm$^{-1}$, while in glycerides the same displace at 1737 cm$^{-1}$. At the end of the first stage in the reaction system there are monoglycerides, diglycerides, free glycerol and potassium phosphate.

During the second stage a process of solvolysis (simultaneous depolymerization and dissolution) of PET was carried out. The solvolysis reagents are both glycerides and glycerol. The depolymerization of the waste PET is represented by the chemical reactions of Scheme 2. It is considered that the process is completed after full homogenization of the reaction system.

For the purposes of the analysis, samples were taken. They were purified by twice washing with water, which is a solvent for both glycerol and potassium phosphate. They are wax-like substances with a yellowish-brown color. The chemical bonds in the samples were investigated by FTIR spectroscopy.

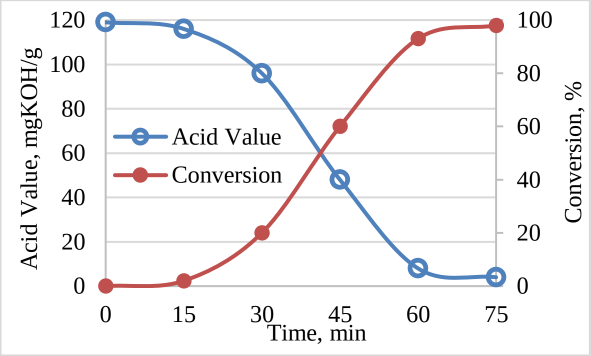
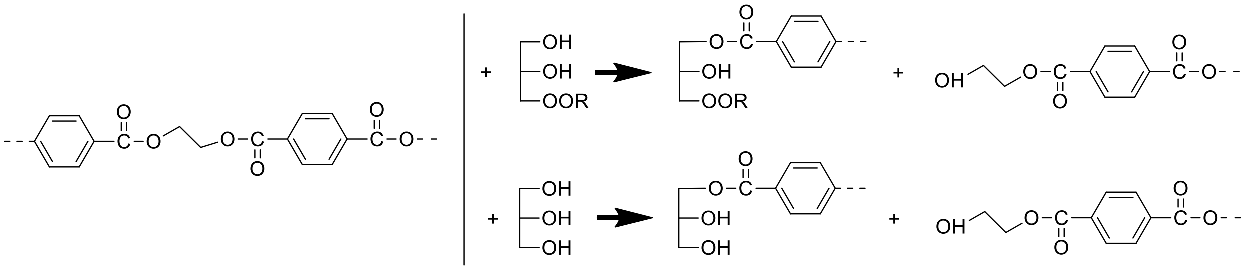
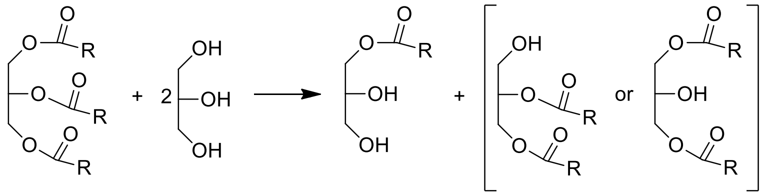


**Fig. 1.** Change of acid value and conversion during reaction time.



**Scheme 2**. Solvolysis of PET with monoglycerides and glycerol



**Scheme 3**. Preparation of glycerides from sunflower oil and glycerol

The simultaneous presence of long hydrocarbon bonds (2926 - $\nu_{as}CH_2$; 2854 - $\nu_sCH_2$; 2956 – $\nu_{as}CH_3$ and 2878 cm$^{-1}$ - $\nu_s$ $CH_3$), p-substituted benzene rings (1578 and 1506 cm$^{-1}$), esters (1724 cm$^{-1}$ - $\nu C{=}O$) and hydroxyl groups (3600-3100 cm$^{-1}$ - $\nu OH$), proves the process of depolymerization of PET and obtaining of polyester polyols.

At the end of the second stage in the reaction system there are polyester polyols, mono- and diglycerides, glycerol and potassium phosphate.

The third stage was esterification with phthalic anhydride. Reactions were followed with AV. Samples were taken every 30 min to determine the AV.

In the prepared alkyds potassium phosphate was still present as a contaminant. For the purposes of the analysis, samples were taken. They were purified by twice washing with water, which is a solvent for potassium phosphate. The samples were named Alk-1S12 and Alk-1S20.

### *Preparation of alkyds Alk-RS12 and Alk-RS20*

Reference alkyds were synthesized by a two-stage alcoholysis-esterification method. The first stage was alcoholysis of unrefined sunflower oil and glycerol (Scheme 3).

Monitoring of reaction was made by methanol test every 15 min.

The second step was esterification with phthalic anhydride. In order to provide a structure identical to that of Alk-1S12 and Alk-1S20, ethylene glycol was added. The quantity was calculated to correspond to the amount of added PET (Table 3). The condensation process was followed by the acid value. For the purposes of the analysis, samples were taken. They are viscous liquid substances with light brown color.

### *Study of alkyds structure*

Chemical bonds in alkyds were established by FTIR spectroscopy (Fig. 2.).

It is visible that in all spectra the doublet at 1601 and 1581 cm$^{-1}$, which corresponds to o-substituted Ar-rings, appeared. Some absorption bands were registered only in the spectra for Alk-1S12, and Alk-1S20. They were: 1412 cm$^{-1}$- δCH$_2$; 1136 -δ(C-O-C) in esters, 875 and 728 for γ =(C-H) in p-substituted Ar-rings. These bands correspond to the bonds in the ethylene terephthalate units.

Results from FTIR spectroscopy were confirmed by the $^1$H NMR analysis. In the 1H NMR spectra of Alk-1S20 and Alk-RS20 the following signals appeared: δ 0.89 ppm for protons in the CH$_3$; δ 5.35 – 5.37 ppm for vinyl protons in CH = CH; δ 7.5-7.9 ppm for aromatic protons of the o-phthalate esters; δ 3.6-4.0 ppm corresponding to methylene and methine protons in the CH$_2$OH and CHOH groups; multiplets at δ 4.3-4.4 and δ 4.1-4.2 ppm for methylene protons in CH$_2$CO-Ar and CH$_2$CO-R groups, δ 5.27 ppm for methine protons in CH-O-CO groups.

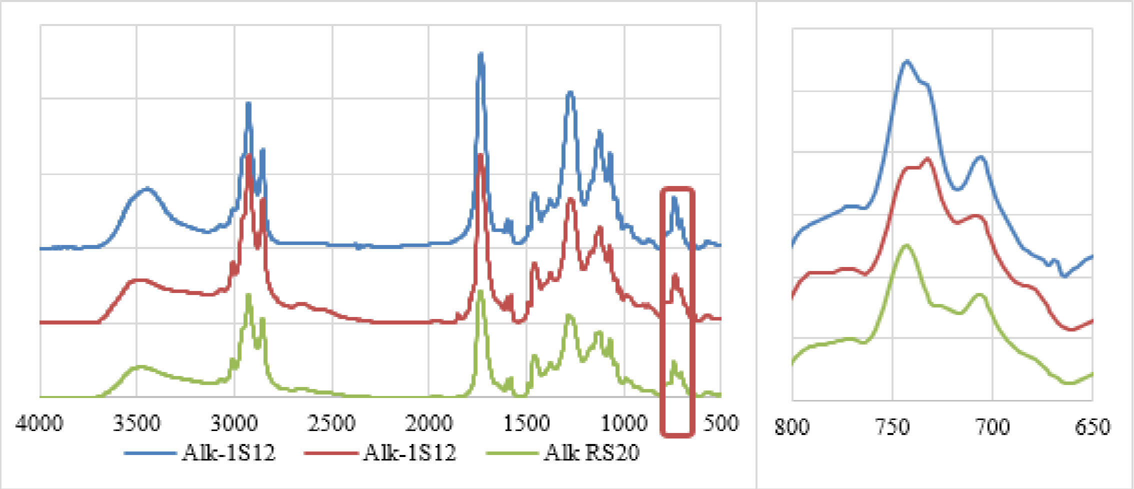


**Fig. 2**. FTIR spectra of Alk G1S12, Alk G1S20 and Alk RS20

In Alk-1S20 spectrum, a signal at δ 8.13 ppm for protons in p-substituted benzene rings appeared. Gathered data confirmed the alkyd structure and the presence of ethylene terephthalate moieties in the alkyds structure.

*Preparation and study of alkyd resins*

From the obtained four medium-oil alkyds, 60% solutions in xylene were prepared. The last contaminant in Alk-1S12 and Alk-1S12 was potassium phosphate. It was removed by filtration.

For accelerated drying of the alkyd resins obtained, 1% of Pb and 0.1% of Co were added. Films were air-dried at 25°C for 24 h and then heated to 110°C for 2 h. Drying degree, hardness and adhesion were evaluated (Table 4).

It is visible that alkyd resins, obtained from Alk-1S12 and Alk-1S20 had better drying degree and higher hardness than reference resins.

Chemical resistance of the films was studied (Table 5).

Results from Table 5 showed that distilled water and sodium chloride solution had no effect on alkyd resins. Acids, however, made films opaque. The strongest effect had the alkali solution. It can be explained with the fact that the alkyds are polyesters which are easily hydrolyzed with hydroxides.

**Table 4.** Drying degree, hardness and adhesion of the films from alkyd resins

| Alkyd resin | Drying degree | Hardness | Adhesion |
|---|---|---|---|
| Alk-1S12 | 5 | 1H | 4б |
| Alk-1S20 | 5 | 1H | 4б |
| Alk-RS12 | 4 | HB | 4б |
| Alk-RS20 | 4 | HB | 4б |

**Table 5.** Chemical resistance of the films from alkyd resins

| Alkyd resin | Solution | | | |
|---|---|---|---|---|
| | Distilled water | NaCl (5 %) | H$_2$SO$_4$ (0.1 M) | KOH (0.1M) |
| Alk-1S12 | a | a | b | c |
| Alk-1S20 | a | a | b | c |
| Alk-RS12 | a | a | b | c |
| Alk-RS20 | a | a | b | c |

a - no change; b - opaque film; c - partially dissolved film

## CONCLUSIONS

All organic substances in the glycerol phase can be used for preparation of alkyds. This utilisation can help stabilizing biodiesel industry. Waste PET was also successfully incorporated into the alkyd composition, reducing the cost of surface coatings - part of the glycerol phthalate was replaced by polyester waste. It was found that the physical properties of alkyd resins are superior to those of reference alkyd resins. Glycerol phase and depolymerization products of waste PET are suitable for manufacturing of alkyd resins, ensuring sustainable development of two expanding industries.

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