

Alkyd resins on the base of waste poly(ethylene terephthalate) and glycerol phase from biodiesel production

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Abstract. One of the most significant environmental challenges in the modern world is the proper management of wastes and by-products. In the present work, we report the results from our research on the possibility of obtaining alkyd resins based on two waste products - poly(ethylene terephthalate) (PET) beverage bottles (among the highest-volume wastes in landfills) and the organic substances of the glycerol phase, obtained as a by-product in the canola oil biodiesel production. After treatment with potassium hydroxide and subsequent neutralization, from the organic substances in the glycerol phase, canola oil fatty acids and crude glycerol (80.6% purity) have been obtained. Two PET glycolysis were carried out by the crude glycerol at two different glycerol/PET ratios. A total of three medium oil alkyds were obtained - two based on PET glycosates, canola oil fatty acids and phthalic anhydride, and one reference alkyd based on canola oil, glycerol, phthalic anhydride, and ethylene glycol. The syntheses were carried out using microwave irradiation. Films from all alkyd resins were prepared, and their physical properties, thermal stability, and chemical resistance were investigated. Results showed that the drying time, hardness, abrasion resistance, thermal stability, and chemical resistance of the PET modified alkyd resins are better than those properties of the reference alkyd resin.

Key words: poly(ethylene terephthalate), glycolysis, canola oil, microwave-assisted depolymerization.

Introduction

One of the most significant environmental challenges in the contemporary world is the proper management of wastes (Dakova et al., 2025; Tsekova et al., 2019). Improper management leads to pollution of air, soil, and water, which causes various health problems for humans and animals, damages ecosystems, contributes to climate change, and results in economic costs (Nikolov & Petrova, 2023; Nikolov et al., 2023; Georgieva et al., 2021). The utilization of wastes by converting them into value-added products is of fundamental importance for the circular economy.

Products used by the coatings industry are of polymer origin, and this industry is attempting to reduce its dependence on petrochemicals. The use of oil-modified polyesters or alkyds is dominant for the surface-coatings industries (Dizman & Ka-

çakgil, 2023). Alkyd resins are commonly used as binders, adhesives, and plasticizers in surface coatings. They have acquired great importance due to their economy, availability of raw materials, biodegradability, durability, flexibility, good adhesion, and ease of application. Alkyd resins are a special family of polyesters synthesized by polycondensation reaction of oils or fatty acids, dibasic acids or acid anhydrides, and polyols with hydroxyl functionality greater than 2. The type of fatty acid used determines the properties of the resin, such as drying time and flexibility. Traditionally, linseed oil, sunflower oil, soybean oil, castor oil, and coconut oil are used in the synthesis of alkyd resin (Kalu et al., 2024).

For environmental reasons, oils used for food should not be used to obtain alkyd resins. Instead, waste oils and non-edible vegetable oils are the

preferred, more sustainable alternatives, as they divert waste from landfills and do not affect food supplies. The literature reports alkyd resins based on mango seed oil (Oragwu et al., 2023), neem seed oil (Das et al., 2021), okra seed oil (Abba et al., 2023), jatropha and sesame seed oils (Mustapha et al., 2022), sesame and sweet almond oil (Mustapha et al., 2023), tomato oil (Ibrahim et al., 2014), etc., but we are not aware of data on obtaining alkyd resins based on canola oil fatty acids. On the European continent, canola oil is a main feedstock for biodiesel production and globally it is among the most used raw materials (Ge et al., 2017). Canola oil contains approximately 40–45% oil (the same as sunflower oil), which is higher than other oil crops, including soybean (about 18–20%). In the second decade of the 21st century, canola constituted ca. 80% of the biodiesel source in Europe (Szczepaniak, 2025).

With the increase in biodiesel production, the quantities of accumulated glycerol phase also increase. Its oversupply has led to an unusual drop in its price (Wang et al., 2024). The utilization of crude glycerol would not only improve the economics and carbon footprint of biodiesel but would also contribute to the transition to a circular economy (Leong et al., 2021; Tomatis et al., 2024; Wang et al., 2024). From the glycerol phase accumulated during the production of biodiesel from canola oil, canola oil fatty acids (COFA) and crude glycerol (CGly) can be obtained, which could be utilized as secondary raw materials for obtaining alkyd resins. The main problem is that the iodine value of canola oil is 100–120 gI₂/100 g, which classifies them as semi-drying or non-drying. In our preliminary studies, it was found that alkyd resins based on CGly with COFA and phthalic anhydride are unable to form air-drying films.

The present work is a continuation of these studies and aims to improve the drying, physical and chemical properties of these resins. A number of studies indicate that this can be achieved by introducing waste PET into the composition of alkyd resins (Al-Sabagh et al., 2016; Haggag et al., 2014; Ouyang et al., 2021; Todorov et al., 2015).

PET bottles for soft drinks are among the most voluminous wastes in landfills. Their utilization not only reduces landfill waste and pollution but also supports the circular economy because the plastic is reused. When included in the composition of alkyd resins, PET replaces part of the phtha-

lic anhydride and ethylene glycol, which are non-renewable resources from fossil fuels and reduces greenhouse gas emissions. It cannot be introduced directly into the composition of alkyd resins; it must first be depolymerized. Most reported PET depolymerizates are obtained at a weight ratio glycol/PET = 2 and above.

In this work, we present the results of our research on obtaining PET depolymerizates with crude glycerol at a weight ratio of glycerol/PET = 1.01 and 2.02 and using them for preparation of alkyd resins based on the obtained glycosates, canola oil fatty acids, and phthalic anhydride.

Materials and methods

Materials

PET was obtained from waste beverage bottles. They were immersed for 1 h in 1% solution of sodium hydroxide to remove surface contamination, washed with water, and dried at 80°C. Consequently, they were ground to flakes of 1.0–1.2 mm size.

The glycerol phase, obtained in the production of biodiesel from canola oil (GPh-A), was provided to us by “Astra Bioplant” LTD, Bulgaria.

Phthalic anhydride (PhA), alkyd resin BALKYD 480 C – 60 MTK (BALKYD), and calcium octoate (10%) were provided by “Orgachim JSC”, Ruse.

Xylene, KOH, phenolphthalein, H₃PO₄, and CH₃OH were produced in Bulgaria and were used without further purification.

Glycerol 95% (Gly), ethylene glycol, cobalt naphthenate (CoNp), zirconium octoate, and methyl ethyl ketoxime were purchased from Aldrich and were used without further purification.

Treatment of the glycerol phase GPh-A

It was carried out in accordance with the methodology described by Hájek & Skopal (2010). Saponification was performed with a methanolic solution of potassium hydroxide, whereby the fatty acid methyl esters (FAMES - biodiesel), fatty acids, mono-, di-, and triglycerides in GPh-A were converted into potassium salts (soaps). Upon subsequent acidification with phosphoric acid to pH=3, a heterogeneous system was obtained. The resulting solid phase of potassium phosphate settles easily and is separated by filtration. In the liquid phase, the main contaminant is methanol. After its evaporation, the liquid phase separates into 2 layers. The upper layer contains mainly higher fatty acids of canola oil and was designated COFA-A.

The lower layer contains mainly glycerol. Neutralization of the glycerol layer with 50% KOH was performed. The obtained product was designated crude glycerol (CGly-A).

Preparation of Alk-1 and Alk-2

A modified 700W microwave oven DAEWOO KOR 6485 (17 L) was used for the preparation of alkyds Alk-1 and Alk-2. First, a microwave-assisted glycolysis of PET by CGly-A has been conducted. Pre-calculated amounts of PET and CGly-A were charged into a reaction flask equipped with a reflux condenser. Glycolysis reactions were carried out at atmospheric pressure at a temperature of 230°C, which was maintained at a microwave power level of 300 W. The mixture temperature was monitored with an infrared pyrometer Trotec TP7. The glycolysis time was determined experimentally - the time at which a sample of the glycolysis product remains clear, without traces of unreacted PET flakes after cooling to room temperature. Two glycolysis products, GP-1 and GP-2, were obtained, differing in the Gly/PET ratio (mass ratios 2.02 and 1.01, respectively). For GP-1, the glycolysis time was determined to be 15 minutes and for GP-2 - 20 minutes.

From glycolysis products GP-1 and GP-2, alkyds Alk-1 and Alk-2 were prepared by the following method - after cooling glycolysis products to 150°C, calculated amounts of COFA-A and phthalic anhydride were added, then the reaction mixture is heated again to temperature 170°C (microwave power 252 W) for 15 minutes, after that the temperature was raised to 230°C (microwave power 300 W). The process was followed by the acid value. Reactions were continued until an acid value below 12 mg KOH/g.

Preparation of the reference alkyd Alk-R

In a reaction flask, 52.2 g canola oil, 14.8 g glycerol and 0.6 g KOH were charged. The flask was placed in the microwave oven. Alcoholysis proceeded at microwave power 300 W (temperature 230°C). The end of the reaction was monitored by the methanol test. The obtained monoglycerides were cooled to 150°C. Then 6.4 g ethylene glycol and 35 g phthalic anhydride were added. During the first 15 minutes, esterification was carried out at microwave power 252 W (temperature 170°C) and thereafter at microwave power 300 W (230°C). The process was monitored by the acid

value. The reaction was continued until an acid value below 12 mg KOH/g.

Preparation and study of alkyd resins AR-1, AR-2, and AR-R

Alkyds Alk-1, Alk-2 and Alk-R were cooled to 70–80°C and the calculated amount of xylene was added, so as to obtain 60% solutions. In the alkyd resins AR-1 and AR-2, small amounts of potassium phosphate were still present as a solid phase. It is insoluble in xylene, settles as a solid phase, and is removed by filtration. The following main characteristics of alkyd resins were determined: conditional viscosity (DIN 53211) with an Elcometer 2350 DIN flow cup with a 4 mm hole diameter, density at 20°C, g/cm³ (ISO 2811-1) and color according to the Gardner scale (ISO 4630).

Preparation of films from alkyd resins and testing

To accelerate drying of the alkyd resins, catalysts were added: 0.03 g 6% cobalt naphthenate, 0.3 g 6% zirconium octoate and 0.7 g 10% calcium octoate; 0.2% of methyl ethyl ketoxime was added as an anti-skinning agent. The mixtures were homogenized for about 10 minutes and applied onto: plates of mild steel (low-carbon) for the determination of drying time and hardness; sheet metal - for flexibility and adhesion; glass test tubes - for water resistance and chemical resistance.

The following possibilities were examined: air-drying of the alkyd resins at room temperature in the laboratory at 25°C; drying at temperatures of 80°C and 110°C in a thermostatically controlled ventilated oven; air-drying at 25°C for 1 hour, followed by drying at 110°C for 2 hours. The physical properties were investigated according to standardized methods. Hardness was determined by the Pencil hardness tester (ASTM D3363-05). Adhesion strength was measured by the Cross Hatch Cutter tester (ASTM D3359-17). The flexibility was evaluated using a cylindrical mandrel bend tester (ASTM D522). Abrasion resistance was determined by Ericsen Send Abrasion (ASTM D968 - 17). The alkaline and water resistance were determined according to ASTM D 1647.

Instrumental methods of analysis

Gas chromatography: The composition of the fatty acids was determined by a gas chromatographic system Agilent Technologies 7890A equip-

ped with FID, injector with/without split, and Agilent 7693A autosampler. Capillary column: HP-INNOWAX with polyethylene glycol stationary phase. Injector and detector temperatures: 250°C and 300°C, respectively; carrier gas helium. Column temperature program: 200°C, 2 min; 3°C/min to 210°C; 10 min. The glycerol content in CGly-A was determined according to standard EN 14106.

FT-IR spectroscopy: Spectra were recorded on a Nicolet iS 50 FT-IR spectrophotometer in the range 3996–399 cm⁻¹ at a resolution of 2. Samples were prepared as KBr pellets.

Thermogravimetry (TG): The analyses were carried out using an STA-TG-DSC/DTA F3 JUPITER instrument (NETZSCH, Germany) over the temperature interval 20–500°C, under nitrogen atmosphere at a rate of 10 °C/min.

Results and Discussion

Characterization of GPh-A, CGly-A, and COFA-A

By standardized methods, several main characteristics of the glycerol phase GPh-A were determined (Table 1). Table 1 shows the typical complex composition of the glycerol phase - glycerol,

water, MONG (matter organic non-glycerol), and ash. To obtain quality alkyds, strict stoichiometric ratios are observed; therefore, in this form, the glycerol phase cannot be used. Simplification of the composition was achieved by suitable treatment – saponification of GPh-A with KOH, followed by acidification with phosphoric acid to pH = 3. The following were obtained: a solid phase of potassium phosphate; a light fraction - canola oil fatty acids (COFA-A); and a heavy fraction containing glycerol, water, non-separated fatty acids, traces of phosphoric acid, and potassium phosphate. After neutralization of the heavy fraction with KOH, crude glycerol (CGly-A) was obtained. The composition and some main characteristics of CGly-A and COFA-A were determined by standardized methods (Table 2).

COFA contains 98.3% higher fatty acids. Impurities may result from the incomplete separation of glycerol. It is important to note that the iodine value determined by a standardized method is 110.3 g I₂/100 g, which classifies the fatty acids as semi-drying. By gas chromatography, the composition of fatty acids in COFA-A was determined (Table 3).

Table 1. Main characteristics of the glycerol phase GPh-A.

Characteristic	Value
Glycerol content, wt%	50.5
Water content, wt%	12.4
Methanol content, wt%	8.5
MONG content (FAMES, soaps, fatty acids, mono-, di- and triglycerides), wt%	28.6
Ash content, wt%	2.0
pH of a 20% aqueous solution	9
Density at 20°C, g/cm ³	1.06
Gardner color	8

Table 2. Main characteristics of CGly-A and COFA-A.

Product	Characteristic	Value
CGL-A	Glycerol content, wt%	80.6
	Water content, wt%	12.3
	MONG content, wt%	2.1
	Ash content, wt%	4.6
	Density, g/cm ³	1.21
	Color by Gardner	8
COFA-A	Fatty acids, wt%	98.3
	Other organic compounds, wt%	1.7
	Acid value, mg KOH/g	195
	Iodine number, g I ₂ /100 g	110.3
	Gardner Color	9
	Density, g/cm ³	0.899

Table 3. Composition of fatty acids in COFA-A (wt%).

Fatty acid	Count of C atoms and double bonds	Fatty acids content, wt.%
Myristic	C14:0	0.03
Palmitic	C16:0	5.11
Palmitoleic	C16:1	0.21
Stearic	C18:0	5.12
Oleic	C18:1	59.3
Linoleic	C18:2	22.5
Linolenic	C18:3	9.50
Arachidic	C20:0	0.61
Gadoleic	C20:1	1.23
Behenic	C22:0	0.57
Erucic	C22:1	0.95
Lignoceric	C24:0	0.16

Knowledge of the fatty-acid composition enables calculation of the following three important characteristics for COFA-A: (i) the average molecular mass of the free fatty acids - 283.6 g/mol; (ii) the iodine value of the free fatty acids, determined by the method of Kyriakidis & Katsi-loulis (2000) - 111.6 g I₂/100 g, which classifies the fatty acids as semi-drying; and (iii) the drying index - 41.5, which defines the fatty acids as non-drying.

Theoretical calculation of the alkyd compositions

The theoretical determination of the alkyd compositions is carried out to obtain quality alkyds and to avoid gelation processes. "K alkyd constant system" was used for the formulation

calculations of the alkydes. Three medium-oil alkyds were determined. Alk-1 and Alk-2 were obtained from CGly-A, COFA-A, PhA, and different amounts (10 and 20 g, respectively) of waste PET. Alk-R is a reference alkyd, obtained from canola oil, glycerol (95%), and phthalic anhydride (Table 4). To achieve identity in the structure of the alkyds, ethylene glycol was introduced in an amount corresponding to the ethylene units in PET.

Important characteristics for alkyds were calculated: the Patton's constant ($K = 1.1$) and the excess of hydroxyl groups $R = 25\%$. When determining the required quantities of the starting raw materials (COFA-A and CGly-A), it is taken into account that COFA-A contains 1.7% glycerol and CGly-A contains 2.1% MONG (Table 2).

Table 4. Composition of alkyds Alk-1, Alk-2 and Alk-R.

Composition	Alk-1	Alk-2	Alk-R
Gly, g			14.8
Canola oil, g			52.2
CGI, where	24	24	
Gly, g	19.3	19.3	
MONG, g	0.5	0.5	
COFA, where	51	51	
FFA, g	50.1	50.1	
Gly, g	0.9	0.9	
PET, g	10	20	
EG, g	3.2	0	6.4
PhA, g	27.5	20	35

Preparation of alkyds Alk-1 and Alk-2

To obtain Alk-1 and Alk-2, the following two consecutive steps were carried out:

First step - PET glycolysis with CGly-A. This process is necessary because PET cannot be direc-

tly introduced into the alkyd composition due to the lack of a common solvent and incompatibility with the other starting products. For modification with PET, it is necessary to degrade the polyester waste to such an extent that it dissolves in the

depolymerizing reagent and a homogeneous solution is obtained. In the present work, a glycolysis of flakes from PET soft-drink bottles with CGly-A was carried out. The process is schematically presented in Fig. 1.

As a result of PET glycolysis, two products - GP-1 and GP-2 were obtained, differing in the Gly/PET mass ratio (2.02 and 1.01, respectively).

Samples taken from GP-1 and GP-2 were purified by washing with distilled water to remove unreacted glycerol and potassium phosphate. Hydroxyl values were determined, and FTIR spectra of the purified glycolysis products were acquired. The hydroxyl value was 285 mg KOH g⁻¹ for GP-1 and 239 mg KOH g⁻¹ for GP-2.

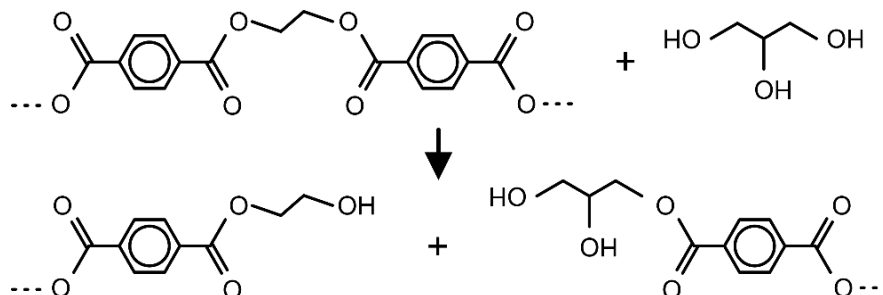


Fig. 1. PET glycolysis by glycerol.

FTIR spectra were recorded to confirm the chemical bonds in the glycosides (Fig. 2). The broad band, observed between 3600 cm⁻¹ and 3100 cm⁻¹, was attributed to the OH group stretching vibration. For GP-1, the intensity is higher, which is an indication of a higher degree of depolymerization. The following bands were also observed at:

- ♦ 2956 cm⁻¹ and 2885 cm⁻¹ for the asymmetric and symmetric stretching vibrations of CH₂, respectively;
- ♦ 1717 cm⁻¹ correspond to C=O stretching vibrations;

- ♦ 1600 cm⁻¹, 1501 cm⁻¹, and 1454 cm⁻¹ correspond to the C=C-C Aromatic ring stretch;
- ♦ 1409 cm⁻¹ for bending vibrations of CH₂ in CH₂-OH;
- ♦ 1276 cm⁻¹ and 1111 cm⁻¹ for the stretching vibrations of the C-O in CH_x-O-CH_x (x=1-3);
- ♦ 1043 cm⁻¹ which is characteristic for the C-O in the CH₂-OH of the glycerol moiety;
- ♦ 730 cm⁻¹ corresponds to -CH out of plane bending for p-substituted aromatic rings.

Hydroxyl values and FTIR spectra confirm that the glycoside products GP1 and GP-2 are polyester polyols.

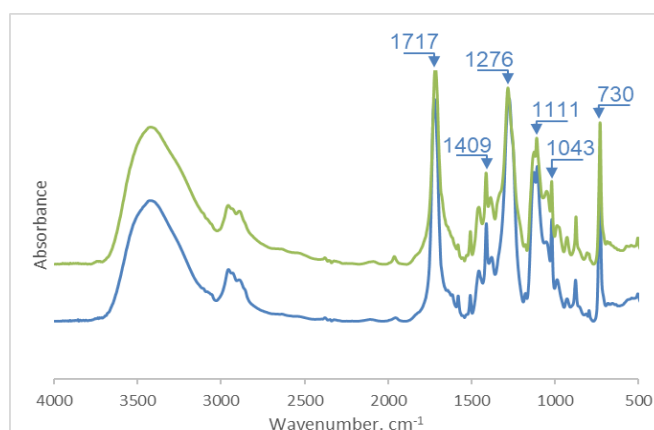


Fig. 2. FTIR spectra of the purified glycolysis products GP-1 (blue) and GP-2 (green).

In glycosates GP-1 and GP-2, in addition to polyester polyols, there is free (unreacted) glycerol and potassium phosphate. The latter was not

removed because it was found to affect the reaction rate. GP-1 and GP-2 were obtained in 15 and 20 minutes, respectively. For comparison, micro-

wave PET depolymerization was carried out using pure glycerol under the same conditions (weight ratio Gly/PET=2.02 and microwave power 300W), and it was found that the glycolysis time was over 60 minutes. Although we are not aware of any literature data that potassium phosphate is a catalyst, similar potassium compounds, such as potassium carbonate and potassium sulfate, have been used as catalysts for PET glycolysis. In addition, it is possible that potassium phosphate can create hot spots under microwave irradiation conditions. In this case, it is important to note that potassium phosphate has no adverse effects and no purifica-

tion of the crude glycerol CGly-A is necessary for carrying out PET glycolysis.

Second step - esterification. From the glycolysis products GP-1 and GP-2, alkyds Alk-1 and Alk-2 were obtained. After cooling to 150°C, calculated amounts of COFA-A and phthalic anhydride were added to each of the glycolysis products. The beginning of esterification was recorded when reaching a temperature of 170°C. The process is carried out with both polyester polyols and free glycerol. Fig. 3 shows a generalized structure of the synthesized alkyds.

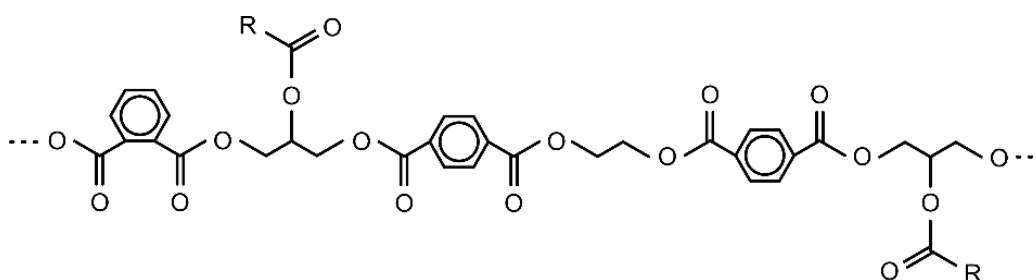


Fig. 3. Generalized structure of the synthesized alkyds

The process was followed by the acid value. The reaction is continued until an acid value below 12 mg KOH/g. Results showed that for alkyd Alk-R, the process proceeded for 50 min. For the PET-modified alkyds, the esterification time decreased; the more PET was introduced, the shorter the esterification time. The process for Alk-2 was completed in 40 min.

Preparation and study of the alkyd resins AR-1, AR-2, and AR-R

Some main physicochemical properties of the obtained alkyd resins were determined (Table 5). From the results in Table 5, it can be seen that the acid value of all three alkyd resins is within the range that will ensure corrosion resistance when applied as surface coatings. The density and visco-

sity of the PET-modified alkyd resins AR-1 and AR-2 are higher than those of the reference AR-R. These differences can be explained by the structure created by the introduced p-substituted benzene rings by the PET modification. In AR-R, there are only o-substituted benzene rings, which, due to steric hindrance, create a looser structure than that formed by the p-substituted benzene rings of PET in AR-1 and AR-2. When comparing the basic physicochemical properties of the alkyd resins with those of the commercial resin BALKYD 480 C-60 MTK, it can be seen that the main difference is in the color. AR-1, AR-2, and AR-R have a brown color, because canola oil and COFA are brown, whereas the commercial resin based on sunflower oil is pale yellow.

Table 5. Main physicochemical properties of the alkyd resins AR-1, AR-2, AR-R, and of the commercial resin BALKYD 480 C - 60 MTK.

Characteristic	A-R1	AR-2	AR -R	BALKYD
Acid value, mg KOH/g	4.3	3.8	5.5	<12
Viscosity, Ford Cup, 4 mm at 25°C, s	110	115	105	105
Density at 25°C, g/cm ³	0.988	0.991	0.982	0.985
Gardner color	10	10	10	5

Drying and testing of films from the alkyd resins AR-1, AR-2, and AR-R

For the acceleration of drying, catalysts (driers) are added. The type is determined on the basis of literature data, and the quantity and drying conditions were determined experimentally. It is known (Gorkum & Bouwman, 2005) that the combination of cobalt and lead driers has the best catalytic properties for alkyd resins. From an ecological point of view, in the present work, the lead dryer was replaced with zirconium. Its action was supplemented by a calcium drier, which helps improve various characteristics, such as hardness and gloss. The quantities of the driers were varied in order to obtain optimal results. When a larger amount is used, more densely crosslinked system is formed and curing is facilitated; however, for

ecological reasons, the studies were carried out with the smallest possible amounts of driers, namely: Co – 0.04%; Ca – 0.2%; Zr – 0.3%. 0.2% of methyl ethyl ketoxime was added as an anti-skinning agent. The obtained mixtures were homogenized and applied onto pre-cleaned surfaces. Each test cycle is performed with three specimens. Possibilities were examined for drying at room temperature and drying at elevated temperatures. The films were evaluated as: tacky (t); dry to touch (d); hard (h). It was established that the air-drying ability of all types of resins at room temperature is unsatisfactory - no hard film is obtained after 7 days. Upon heating at 110°C for 1 hour, hard films were obtained from AR-1 and AR-2 (Table 6). From AR-R, hard films were obtained after drying at 110°C for 3 hours.

Table 6. Drying of films from the alkyd resins AR-1, AR-2, and AR-R.

Alkyd resin	Drying at:		
	80°C 1 hour	110°C 1 hour	110°C 3 hours
AR-1	d	h	
AR-2	d	h	
AR-R	t	d	h

The results (Table 6) show that the drying ability of the PET-modified alkyd resins is better than the reference resin.

For evaluation of the physical properties (hard-ness, adhesion, flexibility, abrasion, thermal stability) and of the chemical resistance, the films were dried under the following regime: air-drying for 1 hour followed by drying at 110°C for 5 hours. As shown in Table 7, the films obtained from the PET-modified resins AR-1 and AR-2 have higher hardness than the films obtained from the refe-

rence AR-R resin. This is probably due to the presence of p-substituted benzene rings, which facilitate interactions, and a denser structure is obtained than that formed with the sterically hindered o-substituted benzene rings. The reference resin has lower hardness and lower wear resistance. Regarding adhesion and flexibility on bending, no differences are observed between AR-1/AR-2 and the reference resin. The physical properties of AR-1 and AR-2 do not differ substantially from those of the commercial resin.

Table 7. Hardness, adhesion, and flexibility of films from the alkyd resins.

Alkyd resin	Hardness	Adhesion	Bending test, cylindrical mandrel ¼ inches	Abrasion resistance (mL sand)
AR-1	HB	3 B	passed	1000
AR-2	1H	3 B	passed	1100
AR-R	2B	3 B	passed	800
BALKYD	2H	3 B	passed	1200

Resistance upon immersion in water and chemical resistance of films from the alkyd resins were evaluated in three categories: no change (a);

film becomes opaque (b); partially dissolved film (c). From the results in Table 8, it is seen that all films are resistant to immersion in distilled water

and in 5% NaCl solution. Upon immersion in 0.1 M H₂SO₄, after 24 h, the films of AR-1 and AR-R become opaque. All resins are weakly resistant to alkalis.

The thermal stability of the three types of resins was investigated by the DTA method. Thermal degradation was carried out at a heating rate of 10°C/min in a nitrogen atmosphere. From the comparison of thermal stability (5% mass loss), it

was established that the highest thermostability is for AR-2 (270°C) and the lowest for AR-R (220°C).

Results showed that: the films from alkyd resins AR-1 and AR-2 outperform the reference resin AR-R with respect to drying ability, hardness, abrasion resistance, chemical resistance, and thermal stability; they do not differ substantially from those of the commercial resin.

Table 8. Resistance upon immersion in water and the chemical resistance of films.

Alkyd resin	Resistance upon immersion in			
	Distilled water	NaCl (5%)	H ₂ SO ₄ (0.1M)	KOH (0.1M)
AR-1	a	a	b	c
AR-2	a	a	a	b
AR-R	a	a	b	c
BALKYD	a	a	a	b

Legend: no change (a); film becomes opaque (b); partially dissolved film (c).

Conclusions

Alkyd resins were obtained and studied on the basis of two waste products - poly(ethylene terephthalate) from beverage bottles and the organic substances in the glycerol phase separated as a by-product in the canola oil biodiesel production. This study shows that these waste products can be used as secondary raw materials in the production of alkyd resins. The films from the PET-modified alkyd resins have improved drying ability and increased hardness and abrasion resistance, as well as increased thermostability and chemical resistance compared to the reference resin. The work has environmental and economic significance. An opportunity is created to utilize waste PET and the glycerol phase obtained in the canola oil biodiesel production, which can contribute to better waste management. The cost of alkyd resins is reduced due to the use of two waste products. Glycerol is replaced with crude glycerol, and waste PET replaces part of phthalic anhydride - a raw material obtained from non-renewable sources. In the case of microwave heating, the formation of alkyd resin results after about 1 hour (with conventional heating, the reaction duration ranges from 8–10 hours), which leads to savings of energy and time.

References

Al-Sabagh, A.M., Yehia, F.Z., Esha, G., Rabie, A.M., & ElMetwally, A.E. (2016). Greener routes for recycling of polyethylene terephthalate. *Egyptian Journal of Petroleum*, 25, 53–64.

doi: [10.1016/j.ejpe.2015.03.001](https://doi.org/10.1016/j.ejpe.2015.03.001)

Abba, A., Umar, K.J., Hassan, L.G., Yakubu, M.K., Alkali, M., & Umar, M.F. (2023). Characterization of Alkyd Resins Prepared from Okra Seeds Oil with Two Polybasic Acids. *Equity Journal of Science and Technology*, 9(2), 34–42.

Das, P., Sharma, N., Puzari, A., Kakati, D.K., & Devi, N. (2021). Synthesis and characterization of neem (*Azadirachta indica*) seed oil-based alkyd resins for efficient anticorrosive coating application. *Polymer Bulletin*, 78(1), 457–479, doi: [10.1007/s00289-020-03120-8](https://doi.org/10.1007/s00289-020-03120-8)

Dakova, M., Nikolov, B., & Getzova, V. (2025). Paths to Sustainable Development: Ecological (R)evolution. *Ecologia Balkanica*, 17 (1), 112–120. doi: [10.69085/eb20251112](https://doi.org/10.69085/eb20251112)

Dizman, C.L., & Kaçakgil, E.C. (2023). Alkyd resins produced from bio-based resources for more sustainable and environmentally friendly coating applications. *Turkish Journal of Chemistry*, 47(1), 1–23. doi: [10.55730/1300-0527.3511](https://doi.org/10.55730/1300-0527.3511)

Ge, J.C., Yoon, S.K., & Choi, N.J. (2017). Using Canola Oil Biodiesel as an Alternative Fuel in Diesel Engines: A Review. *Applied Sciences*, 7, 881. doi: [10.3390/app7090881](https://doi.org/10.3390/app7090881)

Gorkum, R., & Bouwman, E., (2005). The oxidative drying of alkyd paint catalysed by metal complexes. *Coordination Chemistry Reviews*, 249, 1709–1728. doi: [10.1016/j.ccr.2005.02.002](https://doi.org/10.1016/j.ccr.2005.02.002)

- Georgieva, E., Velcheva, I., Yancheva, V., Stoyanova, S., Vasileva, T., Bivolarski, B., Todorova, B., & Iliev, I. (2021). A Review on Multi-Biomarkers in Fish for the Assessment of Aquatic Ecosystem Contamination with Organic Pollutants. *Ecologia Balkanica*, 13 (2), 321-330.
- Haggag, K., Elshemy, N.S., & Niazy, W. (2014). Recycling of Waste PET into Useful Alkyd Resin Synthesis by Microwave Irradiation and Applied in Textile Printing Research. *Journal of Textile and Apparel*, 18(1), 80-88. doi: [10.1108/RJTA-18-01-2014-B010](https://doi.org/10.1108/RJTA-18-01-2014-B010)
- Hájek, M., & Skopal, F. (2010). Treatment of glycerol phase formed by biodiesel production. *Bioresource Technology*, 101, 3242-3245. doi: [10.1016/j.biortech.2009.12.094](https://doi.org/10.1016/j.biortech.2009.12.094)
- Ibrahim, K.A., Abu-sbeih, K.A., Al-Trawneh, I., & Bourghli, L. (2014). Preparation and Characterization of Alkyd Resins of Jordan Valley Tomato Oil. *Journal of Polymers and the Environment*, 22(4), 553-558. doi: [10.1007/s10924-014-0664-9](https://doi.org/10.1007/s10924-014-0664-9)
- Kalu, M.K., Emmanuel, M., Chinedu, E.K., Saa-Aondo, M., Yelwa, J.M., Kenneth, R., Haruna N.A., & Shehu, Z. (2024). Current State of Alkyd Resin Synthesis and Characterization, Extracted from Vegetable Oils. *Asian Journal of Current Research*, 9(2), 1-16. doi: [10.56557/ajocr/2024/v9i285](https://doi.org/10.56557/ajocr/2024/v9i285)
- Kyriakidis, N.B., & Katsiloulis, T. (2000). Calculation of iodine value from measurements of fatty acid methyl esters of some oils: Comparison with the relevant American Oil Chemists Society method. *Journal of the American Oil Chemists' Society*, 77, 1235-1238. doi: [10.1007/s11746-000-0193-3](https://doi.org/10.1007/s11746-000-0193-3)
- Leong, H., Chang, C.K., Khoo, K.S., Chew, K.W., Chia, S.R., Lim, J.W., Chang, J.S., & Show, P.L. (2021). Waste biorefinery towards a sustainable circular bioeconomy: a solution to global issues. *Biotechnology for Biofuels and Bioproducts*, 14, 87. doi: [10.1186/s13068-021-01939-5](https://doi.org/10.1186/s13068-021-01939-5)
- Mustapha, A.O., Ayoku, H.B., & Amao, H.A. (2023). New Alkyd Resins from Underutilized Indigenous Seed Oils: Synthesis and Characterization. *Karbala International Journal of Modern Science*, 9(2), 216-225. doi: [10.33640/2405-609X.3293](https://doi.org/10.33640/2405-609X.3293)
- Mustapha, A.O., Oladele, S.G., Adisa, S.F., & Afolabi, Y.T. (2022). A Response Surface Methodology to Optimize the Yield of Alkyd Resin from *Jatropha* (*Jatropha Curcas*) and Sesame (*Sesamum Indicum*) Seed Oils Using CaCO₃ as Catalyst. *Turkish Journal of Science and Technology*, 17(2), 475-488. doi: [10.55525/tjst.1090577](https://doi.org/10.55525/tjst.1090577)
- Nikolov, B., Stanchev, G., & Petrova, S. (2023). Bioaccumulation of microplastics in *Pisum sativum* L. – a pot experiment. *Ecologia Balkanica*, 15(1), 215-221.
- Nikolov, B., & Petrova, S. (2023). Are there plant biomarkers for microplastic pollution in soil? A review. *Ecologia Balkanica*, 15(2), 232-245.
- Oragwu, P., Onyebuchi, N.J., Jeremaih, O.A., Enujekwute, C., & Adinnu, G. (2023). Alkyd Resin Synthesis from Mango Seed Oil (*Mangifer Indica*, Anacardiceae). *American Journal of Polymer Science and Technology*, 9(4), 55-62. doi: [10.11648/j.ajpst.20230904.12](https://doi.org/10.11648/j.ajpst.20230904.12)
- Ouyang, S., Xie, Y., Fu, W., Ding Y., & Shen, L. (2021). Preparation of autoxidative water-reducible alkyd resins from waste polyethyleneterephthalate. *Royal Society Open Science*, 8, 202375. doi: [10.1098/rsos.202375](https://doi.org/10.1098/rsos.202375)
- Szczepaniak, I., Olech, I., & Szymańska, E.J. (2025). The Use of Canola for Biofuel Production in the Context of Energy Security - A Systematic Literature Review. *Energies*, 18, 2410. doi: [10.3390/en18102410](https://doi.org/10.3390/en18102410)
- Todorov, N.S., Radenkov, M.F., & Todorova, D.D. (2015). Utilization of crude glycerol and waste polyethylene terephthalate for production of alkyd resins. *Journal of Chemical Technology & Metallurgy*, 50(3), 240-248.
- Tomatis, M., Jeswani, H.K., & Azapagic, A. (2024). Environmental impacts of valorisation of crude glycerol from biodiesel production – A life cycle perspective. *Waste Management*, 179, 55-65. doi: [10.1016/j.wasman.2024.03.005](https://doi.org/10.1016/j.wasman.2024.03.005)
- Tsekova, S., Dalgacheva, V.H., & Atanasova, N.K. (2019). Waste-cluster Relationship on the Example of Regional Waste Landfill in Blagoevgrad. *Ecologia Balkanica*, SE 2, 181-185.
- Wang, H., Li, H., Lee, C.K., Nanyan, N.S.M., & Tay, G.S. (2024). A systematic review on utilization of biodiesel-derived crude glycerol in sustainable polymers preparation. *International Journal of Biological Macromolecules*, 261(Part 1), 129536. doi: [10.1016/j.ijbiomac.2024.129536](https://doi.org/10.1016/j.ijbiomac.2024.129536)

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