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Research Paper

Research on The Possibility to Utilize Crude Glycerol and Waste Polyethylene Terephthalate For Production of Alkyd Resins

Environment Science

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Nikola Todorov — Ph.D. Student; Technical Sciences Faculty at University "Prof.Dr.AsenZlatarov"

DonkaTodorova — assoc. prof. Ph.D.; Head of Ecology and Protection of the Environment Department; Natural Sciences Faculty at University "Prof.Dr.AsenZlatarov"

ABSTRACT

The possibility to utilize two waste products – crude glycerol (CGly) and waste polyethylene terephthalate (PET) for production of alkyd resins was investigated. Flakes, obtained from PET beverage bottles were depolymerized with CGly- a side product by the biodiesel production.Two fractions were separated from the depolymerization product – water soluble (WSF) and water insoluble (WIF).

Two medium oil alkyd resins were obtained from WSF (or WIF), phthalic anhydride, glycerol and mixture of sunflower oil and linseed oil by the alcoholysis method. A reference alkyd resin was synthesized from phthalic anhydride, glycerol and a mixture of sunflower oil and linseed oil. Progress of the polycondensation reaction, wasmonitored by periodically checking the acid number of the reaction mixture.

Films, prepared from alkyd resins solutions in xylene were dried at 25°C. Some of their properties were studied – drying time, hardness and adhesion.

Introduction

PET is a thermoplastic polyester with excellent thermal and mechanical properties. It emerged as the most suitable material for beverage bottles and packing of food and medicines. Recycling of post-consumer poly(ethylene terephthalate) (PET) is a worldwide concern due to its environmental impact and large increasing volume of these materials produced by society. [1,2].

On the other hand, there is a problem with the crude glycerol. It emerged in relation to the exhaustion of petroleum reserves on world scale and the boost of biodiesel production in the 1990's.The production of a tonne of biodiesel gives about 110 kg waste glycerol as side product. The overproduction of crude glycerol made it necessary to search for methods of its utilization [3,4].

There is no data in the literature on the chemical recycling of PET with crude glycerol and further use of the product to obtain alkyd resins.

The present paper reports results, obtained from our researches on the possibility to utilize the products obtained from depolymerization of waste PET with crude glycerol for production of alkyd resins.

2. MATERIALS AND METHODS

2.1. Materials

CGly, sunflower oil and linseed oil were purchased on the market. The PET flakes were prepared from beverage bottles. They were immersed for 1 h in 1% solution of sodium hydroxide to remove surface contamination, washed with water and dried at 80^0C. Glycerol with purity of 99% (Gly), phthalic anhydride (PhA), ethylene glycol (EG), methanol,KOH,xylene, Pb acetate and Co naphtenatewerepurchasedfromAldrichandusedwithoutfurtherpurification.

2.2. Glycolysis

In an1l reactorequipped with mechanical stirrer, Dean-Stark gauge thermometer and inert gas inlet, 366 g CGly (3,2mol-Gly) and 37 g xylene were placed.The mixture was then stirred and heated to 120°C until the full evaporation of the water, contained in CGly. Then 76,8 (0,4 mol) g of waste PET flakes were added and the temperature was increased to 220°C. The glycolysis was carried out at atmospheric pressure for 210 min.

The reactor content was then poured into hot distilled water. The solution was filtered hot. The filtrate was cooled for 8 h at 4°C. The white precipitate thus obtained was filtered and was dried at 40°C in vacuum and denoted as water soluble fraction. The product which did not dissolve in hot water was washedand dried at 40°C in vacuum. It was denoted as water insoluble fraction.

2.3. Preparation of monoglycrides

In an 1l reactor,equipped with mechanical stirrer, thermometer and nitrogen inlet, 120 g (0,14mol) sunflower oil and 80 g (0,09mol) linseed oil were placed. The mixture was heated to 100°C and 47 g (0,51mol) Glyand0,4gpotassium hydroxide (used as catalyst) were placed.The temperature was increased to 200°C. Methanol test was performed every 15 min. The reaction continues until 1 ml of sample totally dissolves in3 ml methanol.

2.4. Synthesis of alkyd resin

It was carried out using the same reactor used for the glycolysis. The amounts of monoglycerides, WSF (or WIF) and the phthalic anhydride were determined so as the alkyd constant K to be in the range **1,05-1,07. The reaction temperature for the first 100 min was kept** 170°C, and then it was gradually increased to 220-230°C.Progress of the polycondensation reaction, wasmonitored by periodically checking the acid number of the reaction mixture.The reaction is stoppedwhenacidnumberreaches value < 10mgKOH/g.

2.5. Analysis and characterization

- **determination of the waste glycerol composition**

The glycerol content in CGlywas determined by gas chromatography [5], the water content – by the method of Karl-Fisher[6] and the ashes content – by burning [7].

- **preparation and testing of alkyd resin films**

The drying degree was determined by Ericsen 415 apparatus [8]. The hardness was determined by Pencilhardnesstester [9].The adhesion strength was measured by Cross Hatch Cutter tester [10].

3.RESULTS AND DISCUSSION

3.1. Preparation of alkyd resins

The alkyd resins were prepared in three stages. The first one was glycolysis of waste PET with CGly.The second one was synthesis of monoglycerides from Gly and a mixture of sunflower and linseed oils. The third one was polyesterificationusing glycolysis products (obtained by the first stage), the monoglycerides (second stage) and phthalic anhydride.

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- **Depolymerization of waste PET with crude glycerol**

Waste PET (colorless transparent flakes) was depolymerized with crude glycerol. By standard methods, the composition of the crude glycerol was determined to be as follows: glycerol 80,5%; water content – 8,5%; ashes – 6,1%. The content of the matter organic non-glycerol (MONG) – methyl esters of fatty acids (FAMEs), free fatty acids (FFAs) and glycerides was calculated as the difference 100- (% glycerol content+% water content+% ashes content).

The depolymerization was carried out in a reactor,equipped with Dean-Stark apparatus, to ensure full water evaporation. Then PET flakes, heated to 170°C, were added. The process was carried out under the following conditions:molar ratio CGly/PET =4, temperature -220°C, process duration 210 min. The product obtained was dark brown homogeneous liquid. It was found in a previous study [11] that impurities in CGly (MONG and salts) accelerate the glycolysis process without being included in the molecules of the depolymerized PET. The glycolysis product is a mixture of polyester polyols, free glycerol, ehtyleneglycol, salts and MONG. Based on solubility in water, two fractions were separated from this mixture – WSF and WIF. The WSF was white solid product.Using GPC, the number average molecular weight was found to be 423g mol^{-1}which corresponds to a mixture of precursor monomers and dimers.WIF was light yellow powder with number average molecular weight of 937 g mol^{-1}.

- **Preparation of monoglycerides**

The second stage is synthesis of monoglycerides from glycerol and mixture of sunflower oil and linseed oil.To achieve air-drying alkyd resin, a mixture of 60% sunflower oil and 40% linseed oil was prepared. The drying index of the mixture was 81,6which ensures fast drying at room temperature and smooth surface. The monoglycerides were obtained at temperature 200°Cin the presence of a catalyst according to the technique described above.

- **Synthesis of alkyd resin**

The third stage is polyesterification of the polyester polyolsand monoglycerideswith phthalic anhydride.Three kinds of medium oil resins were synthesized. In two of them – AR-1 and AR-2, part of the phthalic anhydride and part of the Gly were substituted by WSF or WIF. The resin denoted as AR-R is the reference one (Table 1).

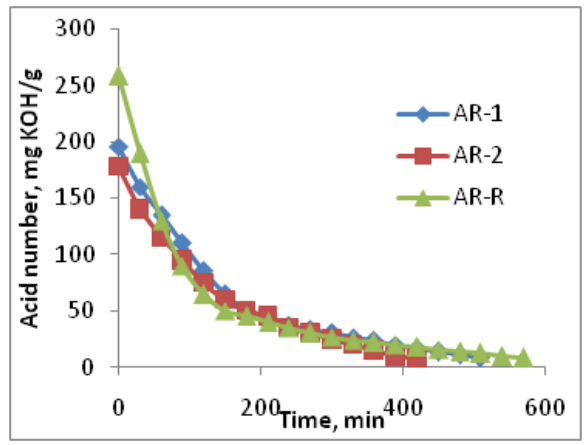
Table1. Denotation and composition of the alkyd resins synthesized

Alkyd resin composition	AR-1	AR-2	AR-R
Sunflower oil, g	120	120	120
Linseed oil, g	80	80	80
Glycerol, g	46	46	81
WSF, g	70		
WIF, g		80	
PhA, g	110	100	145
Alkyd constant K	1,07	1,07	1,07
Excessofhydroxyl groups	1,45	1,45	1,33

In all the three alkyd resins, the contents of sunflower and linseed oils was 47 wt% which classifies them as medium oil resins. Certain excess of hydroxyl groups was provided and the value of the alkyd constant was 1,07 which means that no gelation will occur till the endof the reactions.

The process of polyesterification was controlled by taking samples at 30 min intervals to determine the acid number (Fig.1).

Fig.1. Change of acid number with time during polyesterification



It can be seen that the acid number first sharply decreased to values about 80- 120 mgKOH/g – this is a result of the interaction between the more active primary OH groups of the glycerol with phthalic anhydride. Then the acid number changed at slower rate. The reason for this is that the primary hydroxyl groups had already interacted and the secondary ones have lower reactivity.Molecules mobility also decreased due to increased size and the formation of branches. The interaction proceeds until the acid number reaches values lower than 10mgKOH/g.

The number average molecular weight of AR-1 (M_n), as determined by GPC, was 2950 while that of AR-2 – 3180 and AR-R - 2350 g mol^{-1}.

3.2.Preparation and testing of alkyd resin films

From the alkyd resins, 60% solutions in xylene were prepared. For acceleration of their drying, 1% Pband0,1% Cowere added. Using 50**µ**mapplicator, these solutions were applied on glass substrates.Films were air dried for 72 hours at temperature of 25°C.

The dryingdegree, hardness and adhesion were studied.As can be seen from the results (Table 2), the alkyd resins AR-1 and AR-2 had drying degree better and hardness higher than these of the reference resin. This might be due to p-substituted benzene rings in WSF and WIF, which facilitate the interaction, Thus creating possibility for formation of a structure denser than that with the spatially hindered o-substituted rings.

Table 2. Drying degree, hardness and adhesion of films prepared from the alkyd resins

Alkyd resin	Drying degree	Hardness	Adhesion
AR-1	5	2H	5b
AR-2	5	2H	5b
AR-R	4	1H	5b

Conclusion

Glycolysis of PET waste flakes was carried out using crude glycerol.Two fractions were separated from the depolymerization product – water soluble (WSF) and water insoluble (WIF). Itwasfoundthat theysuccessfullymaybeaddedinthecompositionofalkydresinsbecausetheyarepolyesterpolyolswithappropriatemolecularmassandhave a whiteorlightyellowcolor, respectively.

The introduction of PET depolymerization products into the alkyd resin composition led to the following results:

- Improvedthedegreeof drying and the hardness ofthealkydresins;
- Decreasedthecost, aspartofthe FA andGlyarereplacedbyproductsofglycolysis

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