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Utilization of glycerol phase by synthesis of alkyd-methyl methacrylic copolymers

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Abstract

Glycerol phase obtained from waste cooking oil-based biodiesel production, was utilized. By suitable treatment, crude glycerol (glycerol content 80,8%) and free fatty acids (98,8% content and iodine value 124,3 gI₂/100 g) were obtained from it. Aiming to obtain coatings with good characteristics, modification with MMA was carried out. Composition and structure of copolymers were confirmed by ¹H NMR. Assessment of the main characteristics of the prepared films from the copolymers, showed that they have improved hardness, drying ability and resistance to alkaline substances.

Keywords: waste cooking oil, crude glycerol, surface coating

Introduction

Glycerol phase is a side product from the biodiesel production process. Its deposition in landfills might result in contamination of air, water and soil which could have unfavorable consequences for the biologic versatility. There are data in the literature about the treatment and utilization of the glycerol phase ^[1-2]. One possibility is to synthesize polymers. Researchers have suggested methods for synthesis of polyurethanes ^[3], unsaturated polyester resins ^[4-6], monoglycerides ^[7] and alkyd resins ^[8-9].

However, no information about preparation of grafted copolymers of MMA and alkyd resins on the basis of the organic compounds in the glycerol phase.

The hybrid polymers are very attractive because they have the potential to combine the useful properties of each component. Numerous studies have been carried out for the preparation of such polymers from methyl methacrylate (MMA) and alkyd resin based on linoleic acid ^[10] and from butyl acrylate and alkyd resin based on linoleic and linolenic acid ^[11]. It was found that the hybrid polymers have good adhesion, good drying rate and chemical resistance ^[11].

The aim of the present work is to widen the possibilities for utilization of the glycerol phase, generated as side product from the waste cooking oil-based biodiesel production. For this purpose, alkyds were obtained from the glycerol phase and were then modified with MMA to improve some of their basic characteristics.

Materials and methods

Materials

The waste cooking oil (WCO) discharged after 30 hours of use was supplied by local eating establishment.

Phthalic anhydride (PhA), MMA, methanol, potassium hydroxide, sodium hydroxide, diethyl ether, toluene, were purchased from Aldrich.

Preparation and treatment of glycerol phase GP- WCO

The waste cooking oil was treated by filtering and adsorption with zeolite. A solution of 6g NaOH dissolved in 160g CH₃OH were added to 435 g (0,5 mol) treated cooking oil. Transesterification was carried out in a microwave reactor at 60°C for about 10-15 minutes. The resulting mixture was transferred into a separatory funnel and left for 24 hours. Resulting products were 356 ml biodiesel and 126 ml glycerol phase (GP-WCO).

GP-WCO was first saponified with methanol solution and sodium hydroxide and acidified with hydrochloric acid to pH=3. Solid phase of NaCl and two liquid fractions – crude glycerol (CG-WCO) and fatty acids (FA-WCO) were obtained as described in ^[12].

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Preparation of the alkyds Alk-WCO

Calculated amount of CG-WCO, FA-WCO, PhA and toluene as azeotropic solvent were charged into a round bottomed flask, equipped with mechanical stirrer, thermometer, inert gas inlet and Dean-Stark separator. The temperature at the beginning was 85°C and it was kept until the water from CG-WCO was completely evaporated. The temperature was then raised to 200-220°C. The process of esterification was monitored by acid value determination.

When acid value AV=16 mg KOH/ g was reached, the reaction was terminated, the obtained product was cooled to 80°C, 40 ml of toluene were added, followed by hot filtering. The product was named Alk-WCO.

Preparation of alkyd methyl methacrylate copolymers

The copolymerization was carried out with the same experimental installation. The necessary amounts of Alk-WCO and MMA were placed in a flask. The mixture was heated to 90°C under continuous stirring. Weighted amount of initiator was dissolved in toluene and introduced in the flask dropwise for about 15 min. the interaction proceeded for 5 h at temperature of 95-100 °C.

During the reaction of copolymerization, the conversion was determined every 30 min. For this purpose, a sample of 3 g

was taken, precisely weighted and precipitated with methanol. The precipitated product was filtered, dried and weighted.

Methods of investigation

Some basic characteristics of GP-WCO, CG-WCO and FA-WCO were determined using standard methods (ASTM D 1959 – 85; ASTM D 1980 – 85).

The estimation of the physicochemical characteristics of the films prepared from GC copolymers was performed according to standardized methods, as described in [12].

Gas chromatography: the analyses were carried out on a gas chromatograph system Agilent Technologies 7890A equipped with FID, injector with/without flow separation and Agilent 7693A equipped with automatic sampling.

¹H NMR: the spectra were recorded on a Bruker Avance II+ 600 (600,13 for ¹H NMR and 150,92 MHz for ¹³C NMR) spectrometer with TMS as internal standard for chemical shifts (δ, ppm).

Results and discussion

Initial materials

The initial material for the synthesis of Alk-WCO alkyds was glycerol phase GP-WCO. Some basic characteristics of GP-WCO, CG-WCO and FA-WCO were determined (Table 1).

Table 1: Basic characteristics of GP-WCO, CG-WCO and FA-WCO

Characteristic	Value		FA -WCO	
	GP-WCO	1. CG-WCO	Characteristic	2. Value
Glycerol content, wt. %	1. 40,9	2. 80,8	FFAs content, wt. %	98,8
Methanol content, wt. %	3. 12,5	4.	Acid value, mg KOH/g	191,5
Water content, wt. %	5. 14,8	6. 10,4	Saponification value, mg KOH/g	192,4
MONG content, wt. %	7. 28,6	8. 2,5	Iodine value, gI ₂ /100 g	124,3
Ash content wt. %	9. 0,8	10. 6,3	Density at 20 °C, g/cm ³	0,927
pH	3	11. 6,9	Viscosity, cP	47,5
Gardner color	5	5	Gardner color	6

The composition of GP-WCO is complex. The matter organic non-glycerol (MONG) consists of soaps, biodiesel, fatty acids, mono-, di- and triglycerides. After the treatment, these substances were transformed into fatty acids and separated as individual fraction FA-WCO of quite good quality for technical purposes. The glycerol content in CG -WCO was 80,8% where three kinds of impurities were present: water (which is easily removed by heating), MONG (organic acids) and ash content which is determined mainly by NaCl produced by the treatment of GP-WCO. NaCl remained in CG-WCO due to its solubility in glycerol.

Using gas chromatography, the percentage by mass of the fatty acids in FA-WCO was determined (wt. %): palmitic (C16:0) – 7,01; stearic (C18:0) -3,8; oleic (18:2) - 28,1; linoleic (18:2) -55,2; linolenic (C18:3)-1,81; others (C20-C24) -3,5.

The iodine value and the type of the fatty acids indicate that they can be used to obtain alkyd resins which cannot dry at room temperature.

Preparation of the alkyds Alk -WCO

CG-WCO and FA-WCO were used as initial materials for synthesis of short oil alkyds Alk-WCO. To avoid gelation, alkyds were formulated according to Patton's gel point calculation. Alk -WCO were prepared from:

- FA -WCO - 41 g (0,146 mol) which contained 40,5 (0,145 mol) fatty acids;
- PhA - 60 g (0,405 mol) and

- CG-WCO - 53 g which contained 43 g glycerol, 1,3 g fatty acids and 3,3 g NaCl.

The alkyds Alk -WCO were prepared by the fatty acids method. The process was monitored by measuring the acid value and terminated when acid value measured was below 16 mg KOH / g. The alkyds obtained were cooled to 80°C and diluted with toluene. The product was then hot filtered to remove the main impurity introduced with the crude glycerol – sodium chloride.

Synthesis of grafted copolymers: GC1, GC2 and GC3

Grafted copolymers (GC) with three different compositions (Table 2) were synthesized from Alk -WCO and MMA.

Table 2: Composition of copolymers GC1, GC2 и GC3

Denotation	Alk -WCO	MMA	BPO
GC1	60	40	5
GC2	40	60	5
GC3	20	80	5

The copolymers were prepared under conditions of free radical polymerization of MMA at different ratios AR-WCO/MMA in presence of benzoyl peroxide as initiator.

The grafting of MMA to the alkyds can occur mainly by two mechanisms:

- The acrylic monomer can directly attack the double bonds of the fatty-acid residues of the alkyds;

- The acrylic monomer can bond to the activated methylene group in allyl or diallyl position of the fatty-acid residues.

To confirm the structure of the copolymers, ¹H NMR was used. For this analysis, dry samples of the copolymers were extracted with diethyl ether which is a good solvent of alkyds but not a solvent of poly methyl methacrylate (PMMA). After the removal of PMMA, the ¹H NMR spectrum contained signals, corresponding to alkyds (7,5 and 7,7 ppm for the aromatic ring protons; 5,27 ppm for protons in the CH=CH group; wide signal at 4,1-4,6 ppm corresponding to the alkyds' glycerol structure and signals in the range 0,89 - 2,8 ppm –for the protons in the CH₃ and CH₂ groups of the fatty acid residue), as well as signal at 3,7 ppm corresponding to the protons in –OCH₃ of the MMA units. To confirm the interaction along the double bonds in the fatty residues, the reacted double bonds (RDB) were calculated by the equation [11]:

$$\text{RDB} = [1 - (C_{5,3}/C_{7,6}) / (A_{5,3}/A_{7,6})] \times 100\%$$

Where C and A are the integral areas of the copolymer and the alkyd, respectively, taken from the integral curve.

It was found for the copolymer GC3 that RDB = 90%. The results confirmed that GC1, GC2 and GC3 are grafted alkyd-acryl copolymers.

Evaluation of physico-mechanical characteristics of the copolymers as coating

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Evaluation of the basic characteristics of the copolymers as coatings

The results obtained from the evaluation of the characteristics of the films prepared from the copolymers on glass surface are summarized in Table 3.

Table 3: Basic characteristics of the copolymers GC1, GC2 and GC3

Evaluated characteristics		GC1	GC2	GC3
Drying times, seconds	Dry –to- touch	140	100	60
	Dry –to-hard	480	260	200
Resistance to	Water	a	a	a
	5% NaCl	a	a	a
	0,1M H ₂ SO ₄	a	a	a
	0,1M KOH	c	b	a
Mechanical test	Hardness	1H	2H	3H
	Adhesion	4B	4B	3B

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

It can be seen that the increase of MMA content in the copolymers results in improvement of:

- drying ability of the copolymers;
- hardness of the copolymers;
- the resistance to alkali substances. GC3 showed the best resistance which may be due on one hand to the fact that the methyl groups are hydrophobic and, on the other hand, the methyl group could be steric hindrance for hydrolysis reactions.

Conclusion

A possibility to widen the field of utilization of the glycerol phase obtained as side product by the waste cooking oil-based biodiesel production is shown. It was found that it can successfully be used for synthesis of alkyd-methyl methacrylate grafted copolymers which are suitable for application as surface coatings.

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