Polym. Bull. (2010) 64:739–748
DOI 10.1007/s00289-009-0166-4

ORIGINAL PAPER

Alkyd resins based on waste PET for water-reducible coating applications

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Received: 8 May 2009 / Revised: 30 July 2009 / Accepted: 21 September 2009 /

Abstract Simultaneous glycolysis and neutral hydrolysis of waste PET flakes obtained from grinding post-consumer bottles was carried out in the presence of xylene and an emulsifier at 170 °C. The product was separated from ethylene glycol (EG), water, and xylene by filtration, and was extracted by water at boiling point thrice. The remaining solid was named water insoluble fraction (WIF). The filtrate was cooled to 4 °C, and the crystallized solid obtained by filtration was named water soluble crystallizable fraction (WSCF). These fractions were characterized by acid value (AV) and hydroxyl value (HV) determinations. WSCF and WIF were used for preparation of the water-reducible alkyd resins. Three long oil alkyd resins were prepared from phthalic anhydride (PA; reference alkyd resin) or depolymerization product of the waste PET (PET-based alkyd resin), glycerin (G), fatty acids (FA), and glycol (EG; reference alkyd resin) or depolymerization product of the waste PET (PET-based alkyd resin). Film properties and thermal degradation stabilities of these alkyd resins were investigated. Physical properties (drying times and hardness) and thermal degradation stabilities of the PET-based alkyd resin is better than these properties of the reference alkyd resin.

Keywords Polyethylene terephthalate · Hydrolysis · Glycolysis · Alkyd resin · Water-reducible coating

Introduction

Polyethylene terephthalate (PET) is widely used in packaging applications, especially in water and soft drink bottles industries due to its clarity, light weight,

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and selective gas permeability [1]. PET is one of the extensively recycled polymeric materials. The main motivation for the widespread recycling of PET is its extensive use in plastic packaging applications, especially in the beverage industry [2]. Since PET bottles do not decompose in the nature readily, the disposal of a large amount of PET bottles has caused serious environmental problems. Today, PET bottles have become one of the most valuable and successfully recyclable materials [3]. PET bottle collection in Europe is growing steadily. Post-consumer PET collection rates reach 1,130,000 tons in 2007, a 20% increase over the previous year. In 2007, just about 40% of all PET bottles in the market were collected for recycle [4].

There are four main methods for recycling of waste PET, namely, primary, secondary, tertiary, or chemical and quaternary recycling [5]. The chemical recycling of waste PET can be carried out in many ways, such as glycolysis, hydrolysis, alkolysis, and simultaneous hydrolysis and glycolysis. The aim of most chemical recycling procedures is obtaining monomers, such as terephthalic acid (TPA), ethylene glycol (EG), and bis(2-hydroxyethyl) terephthalate (BHET). The first two can be obtained by hydrolysis under neutral [6], acidic [7], or alkaline [5, 8, 9] conditions and the last by glycolysis [3, 10] of waste PET. All these methods have recently been reviewed by Karayannidis and Achilias [11]. In addition, BHET and monohydroxyethyl terephthalate (MHT) were obtained by simultaneous application of glycolysis and hydrolysis [12].

Waste PET can be depolymerized by glycolysis to obtain oligomeric diols such as bis(2-hydroxyethyl) terephthalate dependent on process conditions. The PET glycolysis products were used for the synthesis of saturated and unsaturated polyesters [13–15], polyurethanes [16, 17], coating materials [18, 19], and additives [18]. But there is no report on using of simultaneous hydrolysis and glycolysis products of waste PET for synthesis of different polymers, such as coating materials, polyesters, and additives.

A fully formulated paint is a complex system which comprises pigments and a variety of additives that vary with the final demands of the coating. These components are dispersed in a fluid continuous phase that may be aqueous or non-aqueous, and which contains a polymer either as a solute or as a colloidal dispersion. This continuous phase is known as the binder and largely determines the character of the coating. It should, however, be emphasized that although solvent-based coatings are still used; the increasing attention to environmental preservation by health and safety agencies has led to an important growth in the development and adoption of water-based resins [19]. One of the largest concerns for the coating industry is to reduce volatile organic compounds (VOC). Water-borne paints are the most practical and effective solution. All classes of traditional paints are currently being converted into water-borne paints [20]. Alkyds, synthetic resins widely used in surface coating industries, are polyesters synthesized from the reaction between polyhydric alcohols, such as glycerol and dibasic acids or their anhydrides such as phthalic anhydride [21]. Alkyd resins can be made water-reducible. The free acid functionality of alkyds are neutralized with amine compounds such as triethylamine (TEA) for preparing of the water-reducible alkyds [22–24].

In the present study, we report the results from our investigations on the possibility for using simultaneous hydrolysis and glycolysis products of waste PET in water-reducible alkyd resins manufacturing.

Experimental

Materials

Waste PET flakes obtained from grinding post-consumer bottles were sieved to obtain a 10–20 mesh fraction. Tween 60 (polyoxyethylene sorbitan monosteriate) was obtained Sigma. This viscosity average molecular weight (Mv) was found to be 3.7×10^4 [6, 12]. Technical grade fatty acid [FA; Sylfat 2S, iodine value (IV) 155, acid value (AV) 197] was used in the preparation of alkyd resins. Phthalic anhydride (PA), glycerin (G) and EG were obtained from Merck.

Simultaneous hydrolysis and glycolysis reactions of waste PET

In previous study, simultaneous glycolysis and neutral hydrolysis of waste PET with constant amount of EG and increasing amounts of water (1 mol EG, 0–13 mol H_2O per mole PET) was carried out at 170 and 190 °C. The oligomeric intermediates products from waste PET were obtained by application of simultaneous glycolysis and hydrolysis [12]. In this study, simultaneous glycolysis and neutral hydrolysis of waste PET was carried out in the presence of xylene and an emulsifier at 170 °C. Reaction conditions were determined, according to the required properties (AV and HV) of the product. The procedure of the application of simultaneous glycolysis and hydrolysis was given as follows.

The reactions were carried out in 1 L stainless steel pressure reactor equipped with a stirrer, temperature control system, and cooling coil. The temperatures of 170 °C were attained in 1 h and the reaction was continued for 1½ h. The charges consisted of 100 g of PET and 31 g EG (corresponding to a molar ratio of 1/1 based on the molecular weights of the repeating unit of PET and EG), 250 mL xylene, 0.5 g of Tween-60 surfactant, 1 g of zinc acetate catalyst, and 90 g water (approximate molar ratio of H_2O/PET of 10/1). After the reaction, the reactor was cooled to room temperature in 15–20 min by circulating water through the cooling coils and immersion in running water. The powder product was separated from EG, water, and xylene by filtration, and was extracted by 1 L water at boiling point thrice. The remaining solid was named water insoluble fraction (WIF). The filtrate was cooled to 4 °C and the crystallized solid obtained by filtration was named water soluble crystallizable fraction (WSCF). WIF and WSCF were dried under vacuum at 30–40 °C.

These fractions were characterized by AV and HV determinations. HV was determined by acetylation of samples dissolved in pyridine by acetic anhydride, followed by back titration of excess reagent with 1 N NaOH solution [6, 12]. AV was determined by titration of samples dissolved in pyridine with 0.1 N KOH solution. The *Mn* value (number–average molecular weight) of depolymerization product was calculated from HV and AV by the known formula of end group analysis method [25]. The Mn value is calculated from Eq. 1

$$\overline{Mn} = \frac{2 \times 56.1 \times 1000}{\mathrm{HV} + \mathrm{AV}} \tag{1}$$

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Preparation of alkyd resins

Alkyds formulated to have oil content 50% were prepared with phthalic anhydride (PA) glycerin (G), fatty acid (FA), and EG or simultaneous hydrolysis and glycolysis products. The combinations and AV of alkyd resins are shown in Table 1. "K alkyd constant system" was used for the formulation calculations of the alkyd resins [26]. The K constant was 1.05 and the ratio of basic equivalents to acid equivalents (R) was 1.15. The reaction was carried out in a round bottom flask equipping with a Dean–Stark piece, gas bubbler, contact thermometer, and mechanical stirrer system. The temperature of the reaction was kept constant at 200–205 °C. The reactions were followed with AV. Condensation reaction was allowed to continue until the AV of the resin was approximately 50 mg KOH/g. The acid values were determined by titration of samples dissolved in ethanol–toluene with 0.1 N KOH solution. Then, the alkyd resins were neutralized with TEA at 120 °C. The alkyd samples were dissolved in isopropyl alcohol to produce 70% (w/w) solution. The pH was adjusted to slightly alkaline (pH = 8) with 25% ammonia solution. Water (70%, w/w) based on weight of the alkyd was added, and the solution was agitated vigorously [22]. Driers (1% Pb, 0.1% Co based on alkyd) and surfactant were added followed by the addition of water and then agitated vigorously. Films cast by 50 μ applicators from the solutions were heated at 150 °C for 2 h in an oven and their properties were determined.

Testing of alkyd resin films

Drying time was determined by an Ericsen 415/E apparatus, which gave results according to DIN 53150. For hardness, a Konig Pendulum, which gave results according DIN 53157, was used. Adhesion strength of the films was determined by the cross-cut method according to ASTM D 3359-76.

Table 1 Alkyd resins

Symbol of the alkyd resins	Raw materials				AV (mg KOH/g)
	Fatty acid	Polyol	Diol	Dicarboxylic acid	
A-WSCF	FA	G	WSCF	PA + WSCF	50
A-WIF	FA	G	EG + WIF	PA + WIF	53
A-REF	FA	G	EG	PA	50

Abrasion resistance is usually performed with a falling sand abrasion test. Sand is dropped down a vertical tube onto the panel that is mounted at a 45° angle. The results are given as the amount of sand required removing a certain thickness of coating [27]. Abrasion resistance was determined by an Ericsen Send Abrasion Tester, type 2511-11, which gave results according to ASTM 9685.

The chemical resistance of the films, such as alkaline, acid, NaCl solutions, and water resistance, was carried out according to ASTM D 1647 and ASTM D 1308-57. Films were prepared on glass test tubes and these films were heated at 150 °C for 2 h in an oven. Then, the tubes immersed in alkaline, acid, NaCl solutions, and water. The tubes were removed from the solutions after immersion for 1, 2, 3, 5, 7, and 24 h, and the appearances of films were observed [22].

The test to evaluate the solvent resistance of alkyd resins was performed as follows. A piece of absorbent gauze (2 cm × 2 cm) swollen in a solvent was set on an alkyd resin coated on a glass panel [28].

All tests were repeated thrice to confirm the repeatability of the tests.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out by Shimadzu TGA 50A under air at a rate of 5 °C/min with 20 mg of alkyd resins.

FT-IR analysis

The infrared spectra of alkyd resins were taken with Digilab Excalibur-FTS 3000MX model FT-IR spectrophotometer using KBr pellets.

Results and discussion

Simultaneous hydrolysis and glycolysis of waste PET

The simultaneous hydrolysis and glycolysis of waste PET was carried out using EG and H_2O in the presence of xylene and an emulsifier at 170 °C. After the reaction, the product was separated from EG, water, and xylene by filtration, and was extracted by boiling water thrice. The remaining solid was named WIF. The filtrate was cooled to 4 °C and the crystallized solid obtained by filtration was named WSCF. HV and AV of the WIF and WSCF were determined, and these data were used for the calculation of number–average molecular weight (*Mn*) of these products. The properties of the products and reaction conditions are given in Table 2. With application of simultaneous glycolysis and hydrolysis, WSCF was found to be mainly composed of BHET and MHT. In the case of WIF, the product consists of the higher oligomers and the amount of carboxyl ended oligomers in the product increase [12]. As shown in Table 2, HV of the WSCF is higher than HV of the WIF and WIF–WSCF% yield of the product is 60–40%.

Table 2 Conditions of simultaneous glycolysis and hydrolysis reactions and properties of reaction products

Product	Temperature (°C)	Time (h)	PET[a]/H_2O (molar ratio)	PET[a]/EG (molar ratio)	AV (mg KOH/g)	HV (mg KOH/g)	Yield (w/w) (%)	*Mn*[b]
WIF	170	1½	1/10	1/1	250	35	60	394
WSCF					240	240	40	234

[a] Based on the molecular weights of the repeating unit of PET

[b] Calculated from HV and AV

Alkyd resins

Water soluble crystallizable fraction (WSCF) and WIF were used for preparation of the alkyd resins. Three long oil alkyd resins were prepared. The combinations of alkyd resins are shown in Table 1. These alkyd resins were neutralized with TEA at a temperature of about 120 °C. After that deionized water was added to neutral resin. A-WSCF and A-REF resins were obtained as dark brown, clear, and homogen liquid (water-reducible alkyd). A-WIF resin was obtained as an opaque liquid and water phase separated from the alkyd resin after 1 h. That is why A-WIF resin was not used for preparation of the water-reducible coating films.

The FT-IR spectra of original alkyd resin and amine modified alkyd resin are given in Fig. 1. The amine-modified alkyd resin shows an additional band owing to the amine compound at 1,680 cm^{-1} [29].

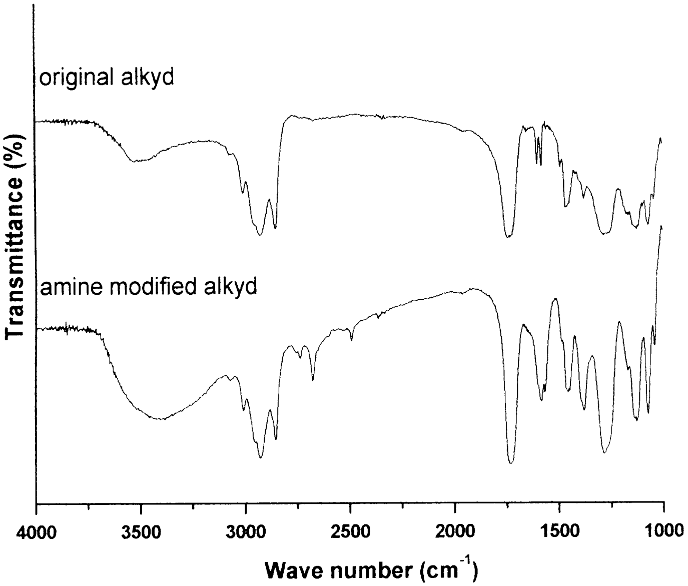

Fig. 1 FT-IR spectrum of alkyd resins

Film properties of the alkyd resins

Determination of drying time of the resins is estimated by adherence or non-adherence of paper or glass beads. There are seven drying stages of this method, and the maximum drying degree is 7. Stage 1 is determined with glass beads and the remaining stages are determined with disks of typewriter paper (loads range from 5 to 5,000 g/cm^2). The glass beads are allowed to remain on the film for 10 s, and the loads on the disks remain for 60 s. As shown in Table 3, drying times and hardness of the PET-based alkyd resin (A-WSCF) is better than these properties of the reference alkyd resin (A-REF). PA was used as dicarboxylic acid in the production of A-REF. Since the carboxyl groups of PA are located in *ortho* position, steric hindrance is observed therefore the reaction occurs more difficult. On the other hand, in PET-based alkyd resins, end groups of the oligomeric intermediates are located in *para* position therefore the reactions proceed easier, and the films that have better physical properties are obtained from these alkyds. Since abrasion resistance determined with falling sand particles depends more on elasticity of the film rather than its hardness [30]; in this case, A-REF shows higher abrasion resistance than A-WSCF. The percentages of the adhesion strength of the alkyd resin films are 100%.

Table 4 shows that all of the resins have excellent alkaline, acid, salt, and water resistance. All of the resins are resistant to alkaline, acid, salt solution, and water until 24 h. Solution or complete detachment from the surface was only observed to alkaline solution after 24 h. The resistance of alkyd films to the representative organic solvents, methanol, toluene, ethyl acetate, and acetone was studied and the results are shown in Table 5. All of resin films showed good resistance to organic solvents. Both of the PET-based resins and reference resins have same properties such as chemical film properties.

Thermogravimetric analysis

Thermal oxidative degradations of the alkyd resins were investigated by TGA under an air atmosphere at a heating rate of 10 °C/min. Results are presented in Fig. 2. The TGA curves indicate that all resins show almost the same degradation behaviors. The A-REF resin showed the worse resistance to thermal oxidative degradation with 75 and 100% weight losses at 375 and 510 °C, respectively. Thermal stability of the A-WSCF was better than A-WIF with weight losses of 75% at 397 °C and 100% at 540 °C. This can be attributed to the presence of oligomeric intermediates, which are bigger aromatic molecules, instead of the PA and EG in the alkyd structure that improve the thermal stability of alkyd resins.

Table 3 Physical properties of the alkyd resin films

Alkyd resins	Drying degree	Hardness (Konig sec.)	Abrasion resistance (mL sand)
A-WSCF	7	105	500
A-REF	6	75	750

Table 4 Alkaline, acid, salt, and water resistance of alkyd resin films

Type of media	Time	Alkyd resins	
		A-REF	A-WSCF
0.1 M NaOH	1	NC	NC
	3	NC	NC
	5	NC	NC
	8	NC	NC
	24	D	D
0.1 M H_2SO_4	1	NC	NC
	3	NC	NC
	5	NC	NC
	8	NC	NC
	24	NC	NC
5% NaCl (w/w)	1	NC	NC
	3	NC	NC
	5	NC	NC
	8	NC	NC
	24	NC	NC
Water	1	NC	NC
	3	NC	NC
	5	NC	NC
	8	NC	NC
	24	NC	NC

NC no change, *D* destroyed due to solution or complete detachment

Table 5 Solvent resistance of alkyd resin films

Alkyd resins	Solvent			
	Methanol	Toluene	Ethyl acetate	Acetone
A-REF	NC	NC	NC	NC
A-WSCF	NC	NC	NC	NC

NC no change

Conclusions

Waste PET flakes were depolymerized by EG and water in the presence of zinc acetate as catalyst. Depolymerization product (WSCF) was used for the preparation of PET-based water-reducible alkyd resin. In this study, long oil alkyd resins were prepared. The film properties and thermal stability of these resins were investigated. The following conclusions can be drawn from the obtained results.

- Physical properties (drying time and hardness) of the PET-based alkyd resin (A-WSCF) are better than physical properties of the reference alkyd resin (A-REF). Since abrasion resistance determined with falling sand particles

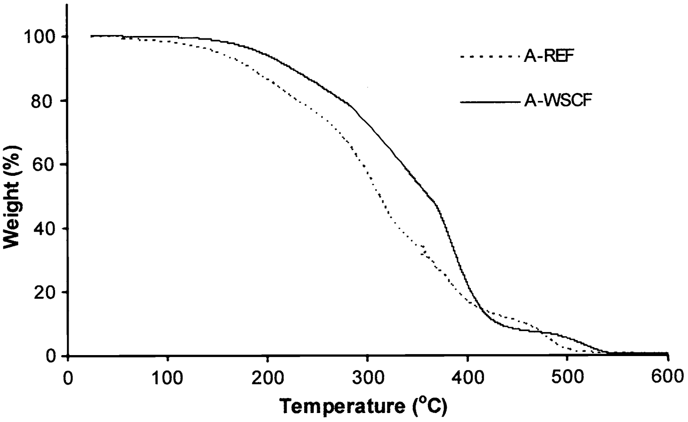

Fig. 2 TGA curves of alkyd resins

depends more on elasticity of the film rather than its hardness; in this case, A-REF shows higher abrasion resistance than A-WSCF.

- The percentages of the adhesion strength of the alkyd resin films are 100%.
- All of the resins are resistant to alkaline, acid, salt solution, and water until 24 h. Solution or complete detachment from the surface was only observed to alkaline solution after 24 h.
- All of resin films showed good resistance to organic solvents (methanol, toluene, ethyl acetate, and acetone).
- Thermal oxidative degradations of the alkyd resins were investigated by TGA under an air atmosphere at a heating rate of 10 °C/min. PET-based alkyd resin was more stable than reference resin.
- The main purpose of this study is investigations on the possibility for using hydrolysis and glycolysis products of waste PET in water-reducible alkyd resin manufacturing. The results show that the thermal stability and physical film properties of PET-based alkyd resins were better than reference alkyd resin.
- As a result, depolymerization product of waste PET (WSCF) is suitable for manufacturing of water-reducible alkyd resins.

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