

Influence of a Catalyst in Obtaining a Post-Consumer Pet-Based Alkyd Resin That Meets Circular Economy Principles

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Research Article

Keywords: Alkyd resin, alcoholysis, glycerol, recycling, PET residue, sustainability

Posted Date: December 15th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-1153463/v1>

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Abstract

The paper studied the influence of a catalyst, comparing it with its traditional counterparts, in the process of obtaining a polyethylene terephthalate (PET)-based alkyd resin from post-consumer beverage bottles and how it consumes raw materials and generates waste. The resin was obtained in two phases: 1) glycerol and soybean oil alcoholysis reaction, a renewable material, for polyalcohol production, and 2) polyalcohol and polyacid esterification reaction to obtain the alkyd resin (reaction via solvent). A lithium octoate catalyst (OctLi) was used, not traditional in the alcoholysis reaction, and a fraction of the polyacid replaced by post-consumer PET at a proportion of up to 24% by weight in the esterification reaction. The OctLi catalyst caused a reaction in 30 min, compared to zinc acetate (120 min) and lithium hydroxide (LiOH, 60 min). Using post-consumer PET in obtaining the alkyd resin also decreased the esterification reaction time by 22% (8% PET), 67% (16% PET) and 72% (24% PET), compared to esterification without PET. The reaction time, considering alcoholysis with OctLi and partial esterification with PET (with 24% PET), was 180 min. Adding alcoholysis time with the LiOH catalyst and esterification without PET raises the reaction time to 600 min. Process water formed during the esterification stage declined by 15% (8% PET), 50% (16% PET) and 77% (24% PET), compared to the reaction without PET. The shorter reaction time resulted in less equipment use and consequent lower energy consumption. Another result was that the alkyd resin obtained with 8% PET was adequate for paint formulations.

1 Introduction

Alkyd resins are used in paint formulations, as finish in the furniture industry and can be combined with different products, such as commercial urea-formaldehyde, melamine-formaldehyde [1], methacrylic acid–maleic acid copolymer synthesized [2], phenolic resins, polyurethanes and others [3–7]. Alkyd coatings are known for rapid drying, good protection against corrosion, high gloss and easy application on untreated surfaces [3, 4, 8].

Traditionally, alkyd resin, an unsaturated polyester resin modified with vegetable oils (renewable raw material) [9], is obtained in two stages: the first involves a reaction between alcohol (glycerol, pentaerythritol or trimethylolpropane) and vegetable oil (fatty acids) to obtain polyalcohol and the second, the reaction of this polyalcohol with a polyacid, generally aromatic (phthalic anhydride, benzoic acid, polyethylene terephthalate) [10–12].

Polyethylene terephthalate (PET) from post-consumer bottles can substitute part of the polyacid [13–15], reducing the use of virgin raw material in the manufacture of alkyd resins [16, 17] used in paint manufacturing [10, 18, 19]. Post-consumer PET can also be used to obtain saturated and unsaturated polyester resins [20–22], adhesive [19, 23, 24] and polyurethane foam [25, 26].

Alkyd resin can be obtained via three procedures: fatty acid process [27, 28], acidolysis [29] and alcoholysis [16, 30, 31].

In the fatty acid process, alkyd resin is obtained in a single stage [27, 32] in which polyol, fatty acid and aromatic polyacid are added and esterification of aliphatic and aromatic acids are concluded simultaneously. Esterification takes place at a temperature between 200 and 250°C [27, 29].

In acidolysis, triglyceride, a component of vegetable oil, is modified with a dibasic acid that replaces one of the fatty acids of the triglyceride molecule. This reaction is applied when poorly soluble polyacids are used in the reactional medium. Since the resulting acidolyzed product (first stage) is more soluble, it results in faster reaction rates than in the second stage. In the second stage of the reaction, polyol is added to form the alkyd resin, at temperatures between 260 and 270°C, more drastic conditions than those of the alcoholysis process [10, 27, 33–35].

In alcoholysis (the first stage to obtain alkyd resin), the transesterification reaction of the vegetable oil occurs, whereby the oil is converted into a monoglyceride (polyalcohol) for the subsequent esterification reaction with polyacids. The alcoholysis reaction occurs at temperatures between 230 and 250°C [10, 27, 33–35].

Products from chemical degradation by post-consumer PET solvolysis are promising raw materials for alkyd resin synthesis. Glycolysis, a specific type of alcoholysis that uses diols as a chemical degradation agent, is most commonly used [2, 16, 19, 21, 36–40]. The physical and chemical properties of the alkyd resins obtained were comparable to those without PET [36].

Another promising raw material in obtaining alkyd resin is glycerol waste, as reported by Todorov, Dzhundzhurova and Todorova [38], who also used it to formulate a sunflower oil/linseed oil mixture. Alkyd resins were obtained by the glycolysis of PET with other ingredients, including hyperbranched polyesters and different fatty acids from vegetable oil, for applications in the coating industry [19].

Amino-alkyd resins were obtained from the reaction between post-consumer PET bottles, propylene glycol (PG) and the catalyst zinc acetate for 6h at 190°C. After glycolysis, short alkyd resins were prepared in oil with phthalic anhydride, glycerin, and fatty acids in coconut oil. Alkyd resins were blended with a commercial urea-formaldehyde and melamine-formaldehyde to prepare the alkyd–amino resins[1].

Hydrolysis [41] and aminolysis [42, 43] are also forms of chemical degradation used to degrade PET, as a stage in obtaining alkyd resin.

Studies have been conducted with two simultaneous PET degradation processes to obtain alkyd resin: glycolysis-hydrolysis [44, 45] and aminolysis-hydrolysis [42]. The aminolysis, aminoglycolysis and simultaneous aminolysis-hydrolysis products from PET waste are suitable for manufacturing both alkyd-based air drying and oven curing paint binder.

To date, reactions have obtained alkyd resin in two stages, which is a classic form, where the chemical degradation of PET is carried out separately and the product is added to totally or partially replace the polyalcohol or polyacid, depending on the formulation used in the alkyd resin syntheses. However, 3 studies were found [10, 15, 18] that performed the reaction to obtain alkyd resin by adding PET directly

into the reactor that synthesizes alkyd resin, with PET degradation occurring concomitantly to this synthesis, partially replacing the polyol or polyacid used in the formulation of the resin.

Kawamura et al. [15] synthesized alkyd resins from PET waste that showed properties similar to those of the traditional ones obtained from ethylene glycol and terephthalic acid monomers. In the first stage of the reaction, pentaerythritol (PE) containing a small amount of ethylene glycol, and soybean fatty acid were added to the reactor in the presence of dibutyl tin oxide. The reagents were heated until reaching the molten state. Post-consumer PET was added to the molten mixture, and the reaction medium heated to 230°C and maintained for 2h until it became transparent. In the second stage, the phthalic anhydride and the rest of the soybean fatty acid were added to the product and heated from 180 to 240°C for 3 hours, a temperature that was maintained until the viscosity and acidity index reached the specified ranges (Viscosity Z; Acid value 7-8). The oil length of the alkyd resin was 55% and R-PET content 10% by weight.

Dullius et al. [10] synthesized alkyd resins with different vegetable oils and fatty acids, and post-consumer PET was added jointly with the polyol. The polybasic acids used were phthalic anhydride and the post-consumer PET was depolymerized in situ. The resins obtained exhibited properties compatible with the resin without the addition of post-consumer PET.

In 2016, Mazurek-Budzyńska, Rokicki, and Paśnik [18] synthesized air-drying alkyd resins, using terephthalic acid from the chemical recycling of PET waste, as an alternative to phthalic anhydride or isophthalic acid. To that end, transesterification was used in two PET stages: in the first synthesis stage, soybean oil was submitted to alcoholysis with pentaerythritol in the presence of the dibutyl tin oxide catalyst at a temperature between 250 and 255°C. In the subsequent stage, the PET reaction occurred with incomplete pentaerythritol esters. The medium was cooled to 220-230°C, PET in the form of flakes was slowly added and the temperature maintained in the 220–230°C range. Under these reaction conditions, PET degradation occurred with the formation of oligomers containing terminal hydroxyl groups.

Catalysts are important ingredients in obtaining alkyd resin. The alcoholysis stage for alkyd resin production is normally catalyzed by Brønsted bases [46, 47], such as lithium [48] and sodium hydroxides [12], calcium [49] and lead oxides [8]. The esterification reaction, which is processed between 190°C and 220°C, starts after alcoholysis.

In general, esterification is controlled by analyzing the acidity index, whose value should be in line with the application of this alkyd resin. If the resin is applied as coating, its acidity index should be around 18 mg of KOH [15, 35, 37, 50, 51].

One of the important points of alkyd resin synthesis is the conversion of oil from its triester to monoester form, which can occur through the alcoholysis reaction in order to incorporate the oil into the resin with the help of a catalyst [38, 49, 52]. The traditional catalysts of transesterification reactions used in alcoholysis reactions are lithium hydroxide [10, 48, 49, 53–55], sodium hydroxide [12, 49, 55], calcium

oxide [49, 55], and lead oxide [8, 49, 56]. Other less common catalysts are zirconium octoate [53] and dibutyltin oxide [18].

Lithium hydroxide (LiOH) is the most widely used catalyst in alcoholysis reactions to produce alkyd resin [4, 13, 27, 32, 48, 49, 51, 53–55]. Studies on the use of metal oxides for alcoholysis reactions have also been conducted [8, 49, 55, 56].

Uzoh and Nwabanne [49] tested the following catalysts for transesterification reactions: sodium and lithium hydroxide, calcium and lead oxide, and calcium carbonate. Alcoholysis occurred at temperatures between 140 and 220°C by a reaction between castor oil and glycerol. Different alcoholysis times were obtained, when 0.5% of the catalyst was used: 60 min with lithium hydroxide; 60 min with lead oxide; 90 min with calcium carbonate; 120 min with sodium hydroxide; and 120 min with calcium oxide. The physicochemical characteristics of the resins formed, such as acidity index, iodine value and saponification value, differed depending on the catalyst used.

Zinc acetate is known as an excellent transesterification catalyst for the glycolysis reaction of PET, but was not applied in alcoholysis reactions for the production of alkyd resins [21, 57, 58]. Organometallic catalysts such as lithium octoate, cobalt and tin are considered catalysts of transesterification [23, 59] and were not used for alkyd resin synthesis with PET. These three octoates are catalysts used by coating companies as curing agents for the paint drying process [51]. Researchers [53] have used zirconium octoate to synthesize alkyd resin as a substitute for lithium hydroxide and the results obtained showed the capacity of this octoate salt to catalyze the alcoholysis of soybean oil and glycerin and prevent oxidation of the oil at high temperatures (290-300°C) in the absence of nitrogen. The alkyd resin was synthesized using the products of alcoholysis and phthalic anhydride, without the addition of PET.

Molero et al. [59] studied metallic octoates (lithium, potassium, calcium, strontium, nickel, zinc and tin) as catalysts of transesterification. The study investigated the glycolysis of flexible polyurethane foam based on polyether with diethylene glycol. The octoates showed different catalytic activities according to the hardness of the cation and the ability to coordinate, with lithium and tin octoates displaying notable catalytic activity.

The hardness of the cation of alkaline octoates determined its potential in forming an alkoxylated metal. Hardness represents how easily a metal ion is deformed in the presence of an electric field; the softer the cation, the more polarizable it is. A harder cation, as observed in lithium, makes the metal less polarizable and allows a higher transesterification reaction rate. A softer cation, such as strontium, exhibits a slower reaction rate. Thus, cation hardness is an important factor in determining the catalytic activity of alkaline octoate salts, increasing the formation of the alkoxide responsible for the nucleophilic attack [59, 60].

The aim of this study was to assess the potential of using a lithium octoate catalyst in the first reaction stage of alkyd resin synthesis (alcoholysis). The use of lithium octoate in the alcoholysis stage, specifically in the synthesis of alkyd resins, was not found in scientific articles, where it is indicated as a drying catalyst [10, 51]. Thus, this article contributes to the scientific community by elucidating the role of

lithium octoate in alkyd resin synthesis. A further objective was to study the production of alkyd resins in a second reaction stage, using residues from PET bottles whose degradation and alkyd resin acquisition occurs in a single stage. These reactions were used to determine the possibility of using fewer inputs (raw materials and energy), less process water and shorter reaction time, in order to meet circular economy concepts and return to the productive cycle of post-consumer products with fewer inputs and less waste generation. The circular economy is an economic system based on business models that replace the “end of life” concept with the reduction, reuse, recycling and recovery of materials in the production, distribution and consumption processes [61].

2 Materials And Methods

2.1 Materials

The reagents used in the synthesis of the alkyd resin are presented in Table 1.

Table 1
Materials used in the reaction to obtain the alkyd resin and their supplier's specifications.

Material	Function in the reaction	Supplier's specifications	Origin
Soybean oil	Triester	Density: 0.93 g/cm ⁻³	Akzo (RJ,Brazil)
Glycerol	Polyalcohol	Concentration: 99.5%; Density: 1.26 g/cm ⁻³	Sigma Aldrich (RJ, Brazil)
Zinc acetate	Catalyst	Concentration: 98.0%; Density: 1.74 g/cm ⁻³	Sigma Aldrich (RJ, Brazil)
Lithium hydroxide	Catalyst	Concentration: 98.0%; Density: 2.54 g/cm ⁻³	Sigma Aldrich (RJ, Brazil)
Lithium octoate LIOCAT® 15	Catalyst	Lithium content: 1.5%; Density: 0.94 g/cm ⁻³	Miracema-Nuodex (SP, Brasil)
Polyethylene terephthalate (PET)	Polyacid	PET post-consumer in the form of flakes; apparent density: 0.37 kg/l *	Wisewood (SP, Brasil)
Phthalic anhydride	Polyacid	Concentration: 98%; Density: 1.53 g/cm ⁻³	Elekeiroz (SP, Brazil)
Xylene	Solvent	Concentration: 99.5%; Density: 0.86 g/cm ⁻³	Norquima (SP, Brazil) Qualival
Methanol	Reagent for analysis	Concentration: 99.8%; Density: 0.79 g/cm ⁻³	Sigma Aldrich (RJ, Brazil)
Phenolphthalein	Reagent for analysis	Density: 1.30 g/cm ⁻³	Sigma Aldrich (RJ, Brazil)

* Density calculated in the study

2.2 Methodology

2.2.1 Raw material characterization

The PET was characterized by Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The soybean oil and glycerol were characterized by FTIR.

Fourier-Transform Infrared Spectroscopy

A 1720-x Perkin-Elmer spectrometer was used for FTIR. The PET was analyzed using the multiple internal reflection (MIR) technique. The spectrum was provided by radiation reflected on the sample surface. The 2 x 4 cm sample was around 1 mm thick. Analysis was conducted with 100 scans per second and 2.00 cm resolution.

The soybean and glycerol were analyzed using a film made of potassium bromide (KBr) pellets, that is, a drop of the sample was placed between the KBr plates. These plates were pressed together and a liquid film formed between them. The sample was submitted to spectral scanning analysis between wavenumbers 4000 cm⁻¹ and 400 cm⁻¹.

Thermogravimetry

The thermal stability of the post-consumer PET used to synthesize the alkyd resin was determined as a function of mass loss with a rise in temperature by TGA in nitrogen purge gas, at a heating velocity of 10°C/min and temperature range of 30 to 700°C.

Differential scanning calorimetry

Heating and cooling cycles in DSC were used to determine the melting and crystallization temperatures, obtained in the second heating cycle. The following conditions were determined: velocity of the first and second heating and cooling was 10°C/min, with a temperature range of 40 to 300°C, nitrogen atmosphere and iodine as standard material.

2.2.2 Alkyd resin synthesis

Alkyd resin was synthesized in the first stage via alcoholysis, in which vegetable oil reacted with glycerol for subsequent esterification (second stage) with phthalic anhydride, and post-consumer PET by carrier solvent, where the catalysts (zinc acetate, lithium hydroxide and lithium oxide) were tested [10].

The route adopted in the present study to synthesize PET-based alkyd resin was not based on the traditional method used by researchers pesquisadores [1, 2, 16, 19, 21, 36–38, 41, 42, 45, 62]. In the traditional method, there is a stage prior to resin synthesis that produces PET oligomers through chemical degradation.

In the present study, the PET oligomers used in resin synthesis were obtained during synthesis, that is, flake was added directly to the reactor after the alcoholysis reaction of the vegetable oil during the esterification stage. Despite its promise, this route has been little studied by the scientific community [10, 15, 18] It optimizes the post-consumer PET-based alkyd resin acquisition process by eliminating previous PET oligomer production before resin synthesis.

Figure 1 presents the general synthesis scheme for alkyd resin processed with and without PET.

The reaction was processed in a 2-liter flask under agitation and inert gas. The carrier gas process consisted of removing the water produced in the synthesis with the help of a solvent. The water vapor formed an azeotropic mixture with the solvent, evaporated and was condensed in a container [27, 29, 54]. Xylene was the solvent selected in order to facilitate the removal of the water produced and help in the reaction conversion [63]. Figure 2 presents the methodology used in the synthesis.

Post-consumer PET was added to the synthesis of the alkyd resin to substitute a fraction of phthalic anhydride in the formulation (Table 2), that is, for each percentage of PET added, the same magnitude of anhydride was removed [10]. The diacids used in synthesis, namely phthalic anhydride and the PET oligomer formed in the glycolysis reaction, were substituted in the same proportion, since both contain the same number of terminal COOH groups.

Table 2
Formulations to obtain alkyd resins (AR), with and without PET

Formulation	Soybean oil (%)	Glycerol (%)	PET (%)	Phthalic anhydride (%)
AR without PET	38 (114g)	23 (69g)	0	39 (117g)
AR 8% PET	39 (117g)	22 (66g)	8 (24g)	31 (93g)
AR 16% PET	39 (117g)	22 (66g)	16 (48g)	23 (69g)
AR 24% PET	39 (117g)	22(66g)	24 (72g)	15 (45g)

The formulation of the alkyd resin was based on technical visits to alkyd resin companies. The amount of catalyst in all the reactions was 0.2-0.5%.

Oil length is another important variable in the formulation of the alkyd resin and is defined as the percentage of non-volatile oil present in the resin. Its amount establishes resin characteristics, which are classified in terms of oil length [48] into three groups: short oil (<45%), medium oil (45–55%) and long oil (> 55%) [48, 51].

Short oil length was used to make better use of the residue, since the shorter the oil length, the higher the proportion of post-consumer PET, resulting in larger amounts of recycled PET incorporated [51], thereby meeting the circular economy principles as closely as possible.

Alkyd resins without PET and with 8, 16 and 24% PET were synthesized. The reaction was conducted until reaching an acidity index of 18 mgKOH/g or less [15, 35, 37, 50, 51].

The alcoholysis reaction was conducted with three catalysts: zinc acetate, lithium hydroxide and lithium octoate, all of which are catalysts in esterification, with lithium hydroxide applied to synthesize the alkyd resin [48, 49, 53] and used as standard. It is important to note that lithium octoate was not used to synthesize the alkyd resin in the presence of PET.

2.2.3 Analyses that accompanied alkyd resin formation

Methanol solubility analysis was used to monitor the reaction time of alcoholysis and the acidity index (AI) of the reactional medium to quantify esterification reaction time.

Analysis of methanol solubility during alcoholysis (first stage of the reaction)

Analysis of methanol solubility aims at assessing oil consumption in terms of its solubilization in a reactional medium, in addition to monitoring and quantifying the reaction time of alcoholysis. The test is based on the principle of methanol insolubility in oil (the onset of the reaction contains soybean oil) and methanol solubility in a monoglyceride (at the end of the reaction, we have the monoglyceride that was formed from the reaction of soybean oil) by visual assessment [12, 29]. If the final solution is murky and with phase separation, the product of the reaction is rejected, and if the solution is transparent, the product is approved [56, 63, 64].

The procedure used to conduct the test involved removing 2ml of reactional sample that was being heated, maintain it at a temperature between 230 and 250°C, periodically transferring it to a 10mL beaker and adding 6mL of methanol until the end of the alcoholysis reaction, that is, until visual solubilization. Next, the beaker was shaken for 1 min and the behavior of the mixture observed. After the alcoholysis reaction reached the desired degree of conversion, that is, the sample solubilized at a proportion of 1:3 in methanol, synthesis with the esterification reaction was carried out [12, 29, 63].

Acidity index in esterification (second reaction stage)

The acidity index of the polymer in the formulation was analyzed in order to monitor and quantify the esterification reaction time, where the carboxyl of the polyacid is consumed (origin of the acid medium) to form the ester. The acidity level of the product in a reaction indicates the degree of conversion or polymerization reached by the time the analysis is carried out. The reaction was conducted until the product attained a value of 18mg KOH/g [15, 35, 37, 50, 51]. The acidity index of the alkyd resin was determined by titration according to ASTM D 465 (2015) [65].

2.2.4 Resin characterization

The alkyd resin was characterized by non-volatile percentage (FTIR), oil length, and acidity index (AI), which was also used to monitor the esterification reaction, and Gardner viscosity. Analysis of the acidity reaction was described in item 2.2.3.

Non-volatile percentage

Alkyd resins are composed of a homogeneous suspension of the polymer (non-volatile) and solvent (volatile). Thus, the non-volatile mass of the resin (%) was determined, that is, the fraction that remained after solvent volatilization.

The amount of non-volatile material in the resin was calculated by oven-drying the sample at 0.5-1.0g per 1h at a temperature of 100°C. First, the resin with the solvent was weighed before it was placed in the oven and after drying, thereby obtaining the solid content in the resin, that is, the non-volatile percentage (NV %). This test was performed according to ASTM D2369 (2020) [66].

Fourier-transform infrared spectrophotometry

Analysis of potassium bromide (KBr) pellets was conducted. One drop of the resin was applied between the KBr plates, which were pressed together, forming a liquid film between them. The final sample without the solvent (sample removed at the end of the esterification reaction, before dilution) was submitted to spectral scanning analysis of wavenumbers between 4000 cm⁻¹ and 400 cm⁻¹. [55, 67, 68].

Oil length

Oil length was defined as the amount of oil present in the non-volatile content [48]. Thus, the amount of solvent was not considered in the calculation. Oil length was calculated by Equation 1 [27].

$$\text{Oil length} = \frac{\text{oil mass}}{\text{alkyd resin-solvent mass}} \times 100 \quad \text{Eq. 1}$$

Analysis of Gardner viscosity

Gardner viscosity for synthesized alkyd resin was determined according to ASTM D1545 (2017) [69]. In this analysis, sample viscosity was calculated by comparing bubble velocity in this sample and in standard viscosity solutions. An amount of the sample was placed in a standard tube with marking spot, and then sealed. An amount of air was trapped to allow a bubble to form in the solution by moving the tube. The tube is inverted, and the bubble rises at a velocity that depends on the viscosity of the solution. Standard Gardner liquid viscosities are expressed in letters and/or numbers, as follows: A5 to A1, according to an A-to-Z scale, and subsequent Z1-to-Z10 scale. The A5 and Z10 tubes represent lower viscosity and higher Gardner viscosity, respectively [69].

The sample of alkyd resin, which is the final product of the reactions, was placed in a tube and bubble velocity was compared with those in standard solutions. The standard tube and the tube with the sample were moved simultaneously. Sample viscosity was obtained when the bubble in the tube with the standard solution rose with the same velocity as the bubble in the tube containing the alkyd resin sample.

2.2.4 Quantification of process water

In the second synthesis stage (esterification), water forms during the phthalic anhydride reaction with the monoglyceride obtained in the first stage. It is known that this process water contains xylene, which is

used to raise the conversion rate [27, 63]. The xylene from the process water of the reaction product was not quantified separately. The waste, denominated process water, is formed by the water mixture resulting from the reaction product and xylene. The process water was collected after the esterification reaction, at the outlet of the reflux system and then weighed.

3 Results And Discussion

3.1 Raw material characterization

The raw materials used in the synthesis of the alkyd resin were characterized. Post-consumer PET, in the form of flakes (shredded post-consumer bottles washed and dried), was characterized by DSC, TGA and FTIR. The soybean oil and glycerol were characterized by FTIR, according to their chemical structure.

Differential scanning calorimetry

The thermal transition values of post-consumer PET are presented in Figure 3. An inflection in terms of glass transition (T_g), two crystallization peaks (T_{CH}) and peak melting temperature (T_m) were determined.

The T_g value (79 °C) of post-consumer PET was similar to that observed by Velásquez et al. [70] (72°C) and Kawamura et al. [15] (75°C), both of whom also worked with post-consumer PET from recycling companies. Badía et al. [71] obtained a T_g of 79°C in PET recycled mechanically in the laboratory. The T_m value (246°C) was also similar to that reported by Velásquez et al. [70] (250°C), Kawamura et al. [15] (245°C) and Badía et al. [71] (246°C).

The two heating crystallization temperature peaks (144°C and 160°C) may refer to the crystalline forms of different PET bottle grades. Post-consumer PET bottles were collected, washed and ground, resulting in flakes. Since these post-consumer flakes originate in different PET manufacturers, there is a strong likelihood of having different PET bottle grades with similar molar masses, but different crystallization temperatures, which could be the cause of the two crystallization peaks [72].

The cooling crystallization temperature was 169°C. According to the literature, the cooling crystallization temperature of PET varies from 158°C [73] to 163°C [72], and the two research groups worked with industrial wastes containing no contaminants, obtained from a bottle manufacturer for the food industry.

Thermogravimetric analysis

The thermal stability of post-consumer PET flakes was determined as a function of mass loss when submitted to different temperatures in TGA analysis. The degradation of post-consumer PET initiated at approximately 375°C and the maximum degradation temperature was 409°C, with a mass loss of 89% at 700°C, values similar to those reported in the literature. According to Miri et al. [74], 83% of PET mass loss occurred between 384 and 442°C and Amaro et al. [75] observed that the mass loss of PET flakes occurred between 395 and 411°C, but did not mention the amount lost.

Fourier-Transform Infrared Spectrometry

Figure 4a shows the peaks characteristic of post-consumer PET, whose main bands are 1714 cm^{-1} for the C=O group; between 1099 and 1244 cm^{-1} for the COOC group; and 723 cm^{-1} for aromatic-H, results also observed in the literature [10, 76, 77].

Figure 4b shows peaks characteristic of soybean oil, whose main absorptions are 2931cm^{-1} and 2857 cm^{-1} (CH_2), 1748 cm^{-1} (C=O in ester), 1466 cm^{-1} (CH_3), and 1169 cm^{-1} (C-O-C) [78, 79]. Figure 4c shows glycerol peaks with the main absorptions of 3385 cm^{-1} (free OH), 2947 and 2889cm^{-1} (CH_2), 1423 cm^{-1} (C-O-H), and 1047cm^{-1} (C-O) [48, 80]. The results of characterization analyses confirm the chemical structures of the raw materials used and were also used to compare and discuss the results of the reactions carried out.

3.2 Catalyst selection for the alcoholysis reaction – first step of the reaction

Alcoholysis time was measured using the solubility test in methanol. A comparison of the reactions that used the different catalysts showed that lithium octoate results in a shorter alcoholysis reaction (30 min). Zinc acetate produced an alcoholysis reaction of 120 min and lithium hydroxide 60 min.

Alcoholysis reactions are normally processed between 1 and 2 hours [49, 51, 56]. Table 3 presents alcoholysis times as a function of type of catalyst used in this and other literature studies, as well as their reagents and reaction temperature. Zinc acetate was the catalyst with the longest alcoholysis time, which is comparable to the times obtained with calcium oxide, magnesium oxide and sodium hydroxide. The lithium octoate used in this study showed a 50% decline in alcoholysis time, compared to the most widely used catalyst (lithium hydroxide), thereby consuming less energy since the reactions occur at the same temperature (around 240°C).

Table 3 Alcoholysis reaction time of this and other studies with different catalysts

Catalyst	Amount used (%m)	Reagents	Reaction time (min)	Reaction temperature (°C)	Reference
LiOct	0.2	Soybean oil and glycerol	30	230-250	This study
LiOH	0.5		60		
AcZn	0.5		120		
CuO-NaOH	-	Palm oil and glycerol	40-60	240	[55]
NaOH	0.5	Castor oil and glycerol	120	140-220*	
CaO	0.5		120		[49]
PbO	0.5		60		
CaCO ₃	0.5		90		
LiOH	0.5		60		
MgO	-	Methyl oleate and glycerol	120	200-250	[81]
LiOH	0.5	Linseed oil or sunflower oil and pentaerythrite	60	240	[51]
LiOH	0.5	Soybean oil or linseed oil or sunflower oil or fatty acid from coconut oil or tall oil fatty acid	60	240	[10]
LiOH	-	tung oil and glycerol	60	240	[32]
CaOH CH ₃ ONa					
LiOH	-	Avocado seed oil and glycerol	-	180-200	[82]
LiOH	0.1-0.5	Camelina oil and glycerol	420	245	[54]
LiOH	0.01-0.1	Sunflower oil and glycerol	300-600	200-300	[48]
LiOH Zirconium Octoate 18%	0.008 (LiOH) 0.199 (Octoate)	Soybean oil and glycerol	-	290-300	[53]

* The researcher did not provide the working temperature.

According to the literature [59, 60], lithium is a harder cation than zinc, resulting in a higher transesterification rate. When lithium hydroxide is used as catalyst, there is an interaction between the Lewis basic site and the alcohol molecule in the transesterification reaction. This acid-base reaction favors a nucleophilic attack by the pair of oxygen electrons of the alcoholic hydroxyl on the carbon of the

carbonyl group of the reagent ester, with consequent formation of a tetrahedral intermediate, giving rise to the other ester molecule and an alkoxide ion. The alkoxide removes one proton from the surface of the catalyst with the formation of another alcohol molecule, thereby regenerating the basic site of the catalytic solid, which becomes once again available to participate in a new catalytic cycle [83].

According to the literature, octoate-based catalysts also form alkoxides [59]. The use of alkaline and earth-alkaline cations promotes greater substitution. However, the more stable the alkoxide of the metal produced, the more difficult the insertion reaction to release the polyol. The regeneration of active species to continue transesterification is the last stage of the mechanism, and the initial stage, that is, the formation of the alkoxide or coordination for insertion, is promoted depending on the type of catalyst (alkaline, earth-alkaline or salt of the transition metal) [59].

Both lithium hydroxide and lithium octoate formed alkoxides, but in the present study lithium octoate was more efficient in catalyzing the alcoholysis reaction. As mentioned before, it can be deduced that the alkoxide formed with lithium hydroxide was more stable, and for this reason, polyol release to the recreational medium was slower, which caused a longer reaction time. In addition, the alkoxide formed when lithium octoate was used exhibited faster catalytic stages.

3.3 Obtaining the alkyd resin – second stage of the reaction

The esterification reaction was followed by the reaction with the alcoholysis product, catalyzed with lithium octoate and phthalic anhydride (without PET) or with 8, 16 and 24% PET. The second synthesis stage occurred at a temperature of 200 -230°C.

Esterification reaction time showed higher acidity values at the onset of the reaction, due to the presence of the polyacid and, as the reaction occurred, the polyacid was consumed and the reactional medium became less acid (lower acidity index) [8, 54].

Figure 5 shows the variation in acidity index (AI) during the esterification reaction, which declined over the course of esterification. The AI value was initially lower for reactions that contained a higher percentage of PET (lower percentage of phthalic anhydride). This may be due to the different reactivities of primary and secondary OH⁻ groups, as reported in the literature [55]. At the onset of the reaction there is a larger amount of primary OH⁻ groups, which are more reactive, and as the reaction occurs, the primary OH⁻ is consumed and the reaction becomes slower. Thus, the esterification rate was higher at the start of the reaction, with a more marked decrease in acid value in all the syntheses with different PET contents. During the reaction, the esterification rate declined due to the secondary OH⁻ reaction, which is less reactive [55, 84].

The esterification times of alkyd resin (AR) without PET and with 8, 16 and 24% PET were 540, 420, 180 and 150 min, respectively. The use of PET to obtain alkyd resin shortened esterification time from 540 min (without PET) to up to 150 mm with 24% PET. The decline in esterification time was 22% with 8%

PET, 67% with 16% PET and 72% with 24% PET, compared to the resin obtained without the addition of PET.

The esterification stage described by Chiplunkar and Pratap [63] was concluded after 360 mm to synthesize alkyd resin (10–22 mg KOH/g) without PET, occurring at a temperature of 240°C, using lead oxide as catalyst. Alkyd resin synthesized (without PET) by Uzoh and Nwabanne [49] used lithium hydroxide in the alcoholysis stage and the esterification stage occurred at a temperature of 200 to 240°C. The reaction occurred until reaching 5 mg KOH/g and lasted 360 minutes. Mazurek-Budzyńska, Rokicki and Paśnik [18] synthesized a PET-based resin containing 25 to 35% PET (flakes made from PET bottles), in which esterification time was approximately 360 min and processed at a temperature of 220–230°C (acidity value not informed). Dullius et al. [10] synthesized an alkyd resin with 14% PET (<18mg KOH/g), from soft drink bottles that were cut into 5 mm²pieces. The authors presented a graph showing esterification time of less than 120 min, using lithium hydroxide as catalyst in the alcoholysis stage, and dibutyl oxide in the second stage of the reaction, with a process temperature of 240°C. In the present study, esterification time was similar to that obtained in the aforementioned research. But, in Dullius et al. [10][7], the decrease in time at this stage was due to the use of an additional catalyst and a temperature 10°C higher than that used in the former investigation. It is important to underscore that individual esterification time varies according to PET content. Table 4 summarizes the parameters and process conditions of the esterification reaction of this and other studies.

Table 4 Parameters to carry out the esterification reaction (2nd stage) of this and other studies.

Study	Alkyd resin	Catalyst	Temperature (°C)	Reaction time (min)	AI (mg KOH/g)
This study	without PET	-	200-230	540	18
	8% PET			420	
	16% PET			180	
	24% PET			150	
Chiplunkar e Pratap [63]	without PET	Lead oxide	240	360	10 - 22
Uzoh e Nwabanne [49]	without PET	-	200-240	360	5
Mazurek-Budzyńska, Rokicki e Paśnik [18]	25 - 35% m PET	-	200-230	360	Acidity value not reported
Dullius et al. [10]	14% de PET	Dibutyl oxide tin	240	< 120	< 18

In addition to the fact that process temperature and additional catalysts influenced reaction time, it is difficult to compare study results, since each investigation used acidity index as final synthesis point, resulting in a longer reaction or not, but not every study reported this index.

Also, in regard to reaction time, xylene was used for two reasons: i) to increase the reaction rate, making the medium more fluid, and ii) to capture the phthalic anhydride that sublimated in the bubble. As previously mentioned, conversion is slower in the esterification reaction, since during synthesis conversion becomes slower and the secondary hydroxyls available for the reaction are less reactive than their primary counterparts. Since this factor also decreases the acidity index, xylene was added to increase the conversion rate [27, 63]. To that end, small amounts of xylene (5 mL) were introduced during synthesis, solvent was added over the course of the esterification reaction and phthalic anhydride (white powder) was added to the walls of the bubble. According to the literature [29], this powder is sublimated and attaches to the walls of the bubble.

The resins synthesized with PET used lower amounts of xylene for reflux due to the shorter reaction time, since the desired AI value was reached in less time, thereby requiring less reflux solvent.

In syntheses without PET, 39% of phthalic anhydride was used and in synthesis with 8, 16 and 24% PET, 31, 23 and 15%. Thus, with a shorter reaction time and less phthalic anhydride, a lower amount of xylene was used. The amount of xylene was not quantified, but its consumption was visually observed.

In the present study, the acidity index, used to determine the end of the reactions, should not be the only parameter to monitor synthesis, given that it is determined by the amount of polyacid used (phthalic anhydride) and initial AI declined as PET content increased, meaning that the acidity value that indicates the end of synthesis (18mg KOH/g) was reached more rapidly. Figure 5 shows that the slope of the curve is scarcely noticeable when 24% PET was used. The reaction was interrupted by the use of Al, giving rise to a resin with a lower than desired Gardner viscosity (in the Y-Z range). It is suggested that future studies on the synthesis of alkyd resins formulated with PET use Gardner viscosity analysis concomitant with the acidity index. In studies that used post-consumer PET [10, 15, 51, 85], the acidity index was also used to indicate the end of the reaction.

Process water quantification

During alkyd resin synthesis, a water by-product is formed, due to the polycondensation reaction of the esterification phase, and monoglyceride reaction (product of the reaction between soybean oil and phthalic anhydride). This water must be removed from the process for the reaction to be converted, altering its equilibrium to form a larger amount of the product [27, 54]. The water removed from the process should be treated before its disposal since it is contaminated by the solvent, namely xylene [86].

The addition of post-consumer PET to obtain the alkyd resin reduced the amount of process water produced, as illustrated in Figure 6. Replacing phthalic anhydride with PET led to a 15, 50 and 77%

reduction in the mass of process water generated during the reaction with the addition of 8, 16 and 24% PET, respectively, findings comparable with the reaction with the addition of PET. No literature data were found to compare these results.

Phthalic anhydride reacts with the monoglyceride, causing the anhydride ring to open, forming a by-product with carboxylic endings, which are consumed during esterification. The hydroxyl group of the monoglyceride (product of alcoholysis) interacts with the ionizable hydrogen of the phthalic anhydride to form a water molecule. The ester is formed by the radical alcohol's binding with the oxygen left over from the hydroxy acid after water formation [49, 53].

The oligomers of the PET formed in the alcoholysis reaction reacted with the glycerol without producing water. Thus, water formation decreased, but was not eliminated, since the reactional medium contained phthalic anhydride, which reacted with the glycerol [14].

Another aspect that contributed to the decline in process water was the lower amount of solvent used as PET was added, as previously described in item 3.3.

3.4 Alkyd resin characterization

Non-volatile percentage

The synthesized alkyd resins were formulated to obtain around 60% of non-volatile (NV) materials, the desired market value for coating applications [35, 51]. The non-volatile percentages of the synthesis products are depicted in Table 5, as well as a number of commercial resins not formulated with the addition of PET. The non-volatile material is responsible for forming the film in paints [8, 66].

Table 5
 Non-volatile percentage of synthesized
 alkyd and commercial resins

Alkyd Resin	NV (%)
Alkyd resin without PET	69
Alkyd resin 8% PET	64
Alkyd resin 16% PET	64
Alkyd resin 24% PET	57
Commercial short alkyd resin (Ashland Resinas, 2020)	68-72
Commercial alkyd resin (Águia Química, 2011)	59-61
Short alkyd resin (Fazenda, 1993)	60

Fourier-transform infrared spectrometry

Figure 7 shows the spectra obtained from the resins with different contents of post-consumer PET. Bands between 721cm^{-1} and 729cm^{-1} indicate the presence of hydrogen atom bonding in the aromatic rings contained in post-consumer PET and in all the resins formed. These bands displaced to 744cm^{-1} and 708cm^{-1} , since they are influenced by the hydrogen band of the CH_3 and CH_2 branches, indicating varying unsaturation of pure soybean oil, becoming more restrictive in the final resins produced [87]. The main bands present in alkyd resins obtained by FTIR are shown in Table 6.

Table 6
Alkyd resin bands synthesized with post-consumer PET.

Band (cm⁻¹)	Characteristic of the band
721-729	H-aromatic
1150-1085	-C-O-C
1395-1365	Twinned dimethyl (CH ₃)
1450-1250	-C-O-H
1603-1507	Aromatic -C-C
1640	-C=C-
1750-1735	Ester –C=O
1738	
1730-1715	
2962 asymmetrical	Aliphatic -C-H
1872 symmetrical	
3000-2840	Aromatic -C-H
2500-3500	Free -O-H
3650-3584	-CH ₂ -OH

For all the compositions, the transesterification reaction was observed by the band displaced from 1743cm⁻¹ [-C=O], characteristic of esters of vegetable oils, to around 1730cm⁻¹ in resins synthesized with different PET contents. The literature [10, 13] reports that PET incorporation in the alkyd resin is confirmed by the band at around 1118cm⁻¹, as observed in the resin spectra produced, that is, the COO group bonded to the aromatic ring. -OH bands (2500-3500 cm⁻¹) also occurred in the resin spectra, indicating that polyol did not react completely [63].

Since each alkyd resin synthesized and shown in the literature [13, 51, 85] has its own properties, there is no common standard to compare them. Those with acidity below 18 are adapted to be used as paint [35, 50, 51], and the alkyd resins obtained in the present study were produced with acidity of around 18 mg KOH/g.

Gardner Viscosity

According to the technical visits to Brazilian paint companies (São Paulo and Rio de Janeiro) and interviews with technicians, the alkyd resin reaction obtained industrially is accompanied by the Gardner viscosity as parameter for final assessment of synthesis, that is, the reaction is performed until the

desired viscosity is achieved. The acidity index is also analyzed. However, in the present study the acidity value and Gardner viscosity could not be assessed simultaneously during synthesis. This viscosity was determined only at the end of the reaction, after the acidity index was obtained. Table 7 demonstrates that the Gardner viscosity values vary. This table also shows the commercial resin values in order to compare the results, which do not contain PET in their composition.

Table 7
Gardner viscosity of alkyd resins obtained in this study and their commercial counterparts.

Characteristics	Gardner Viscosity
Alkyd resin without PET	Z6
Alkyd resin 8% PET	Y
Alkyd resin 16% PET	V-W
Alkyd resin 24% PET	F
Commercial short alkyd resin (Ashland Resinas, 2020)	Z6-Z8
Commercial short alkyd resin (Águia Química, 2011)	Z4-Z5
Short alkyd resin (Fazenda, 1993)	X-Y

In the present article, the synthesized resins with 16 and 24% post-consumer PET were below the viscosity range required for paint companies (Y-Z) [15, 88]. Alkyd resin synthesized with 8% post-consumer PET had Gardner viscosity Y and is therefore within the viscosity range required for paint manufacturers. The esterification reaction of resin synthesized with 8% PET was carried out over a longer time frame, resulting in a resin with higher viscosity, compared to resins synthesized with 16 and 24% PET.

Table 8 presents a summary of the main findings obtained in this study. In the first stage (alcoholysis reaction), reaction time declined by 50% when the lithium catalyst was used. In the second stage (transesterification reaction), the amount of process water, phthalic anhydride and reaction time decreased when post-consumer PET was used.

Table 8 Parameters quantified during alkyd resin synthesis

Results of the 1 st synthesis stage - alcoholysis				
Catalyst				
Alcoholysis time (min)	Zinc acetate	Lithium hydroxide	Lithium octoate	
	120	60	30	
Results of the 2 nd synthesis stage with lithium octoate - esterification				
	Without PET	8% PET	16% PET	24% PET
Amount of phthalic anhydride (% mass)	39	31	23	15
Phthalic percentage used compared to the reaction without PET	-	-8	-16	-24
Amount of water formed (g)	52	44	26	12
Water percentage formed compared to the reaction without PET	-	-15	-50	-77
Esterification reaction time (min)	540	420	180	150
Decrease in reaction time compared to the reaction without PET (%)	-	-22	-67	-72

4 Conclusions

Fewer resources may be used in alkyd resin production in the first alcoholysis stage, with lithium octoate as catalyst, and in the second esterification stage, with the use of post-consumer PET, which meet circular economy precepts.

The lithium octoate catalyst, never previously used in alkyd resin syntheses, was efficient and significantly decreased alcoholysis time. Reaction time was up to 50% shorter, compared with lithium hydroxide, the standard catalyst. A number of factors make the catalyst more efficient, such as cation hardness and the stability of compounds formed during catalysis. A comparison between the lithium hydroxide catalyst and lithium octoate suggests that the former formed a more stable alkoxide. The lower stability of the alkoxide formed with lithium octoate may have released the monoglyceride to the reactional medium more quickly, resulting in a faster reaction conversion.

Another positive point of the study was the insertion of post-consumer PET as reagent to obtain the alkyd resin, which shortened esterification and reaction times by 72, 67 and 22% when 24, 16 and 8% PET, respectively was used. The formulation used to synthesize alkyd resin with PET decreased phthalic anhydride by 8, 16 and 24%.

The use of post-consumer PET obtained from packaging recycling companies is another highlight of this study, since a real sample was used as opposed to other investigations that used PET samples that had no contact with any contaminant or were selected and shredded in the laboratory.

The addition of post-consumer PET in the formulation of alkyd resin also reduced the amount of process water (reactional water and xylene) by 15, 50 and 77%, with the addition of 8, 16 and 24% PET, respectively, when compared to alkyd resin synthesized without PET, thereby decreasing the volume of wastewater treated for disposal in industrial processes. It is important to underscore that alkyd resin obtained with 8% PET was adequate for paint formulations (Gardner viscosity Y).

Due to the low acidity index with a decline in phthalic anhydride mass, it is suggested that the 2nd stage of the reaction to obtain alkyd resin with PET include concomitant analysis of the acidity index and Gardner viscosity. The resins obtained with PET content of more than 8%, which included only analysis of acidity index, resulted in lower viscosities than those required for paint companies (Y-Z).

The experimental procedure adopted proved to be technically efficient in synthesizing alkyd resin and used fewer inputs. The shorter alcoholysis time with lithium octoate was a significant achievement, since it reduced reaction time, and resulted in less equipment use and consequent longer service life, an important factor for industrial production. The use of PET also resulted in less virgin raw material consumption, lower process water production, less reflux solvent expenditure and shorter reaction time.

These elements are attractive from an industrial and environmental standpoint, meet the circular economy precepts, use a more efficient catalyst and integrate a residue in the manufacture of a new product, thereby optimizing the process and adding value to the recycled material.

Declarations

The authors have no relevant financial or non-financial interests to disclose, contributed equally in the elaboration of the paper, read and approved the final manuscript.

Acknowledgements

The authors thank the Research Support Foundation of Rio de Janeiro State (FAPERJ) for the grant awarded to Elaine M. Senra, the Coordination for the Improvement of Higher Education Personnel (CAPES) and the National Council for Scientific and Technological Development (CNPq).

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Figures

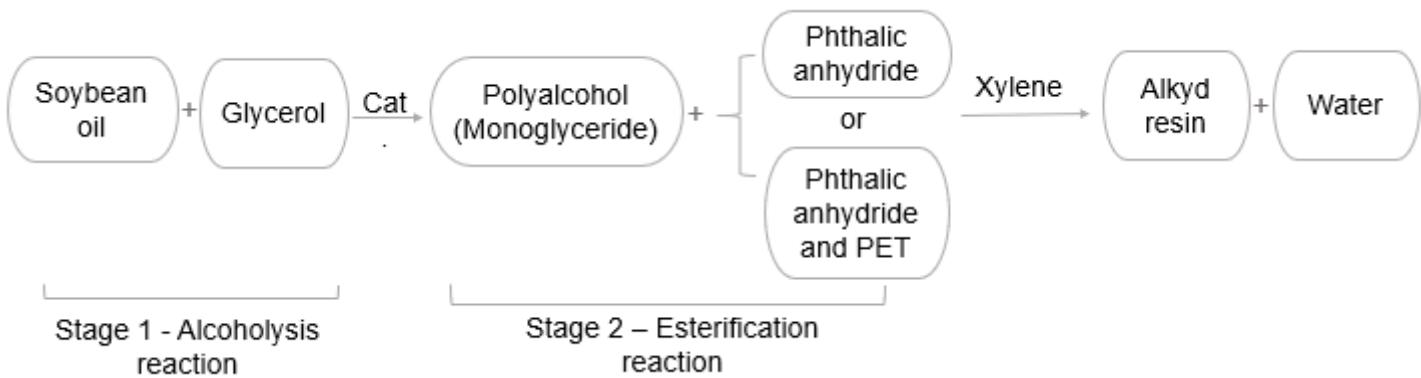


Figure 1

General synthesis scheme for alkyd resin processed with and without PET.

1 | First Stage - Reaction of alcoholysis

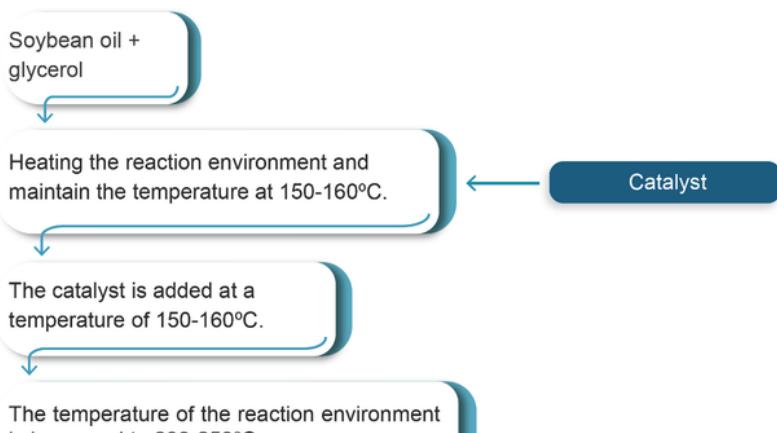


Figure 2

Methodology used in alkyd resin synthesis.

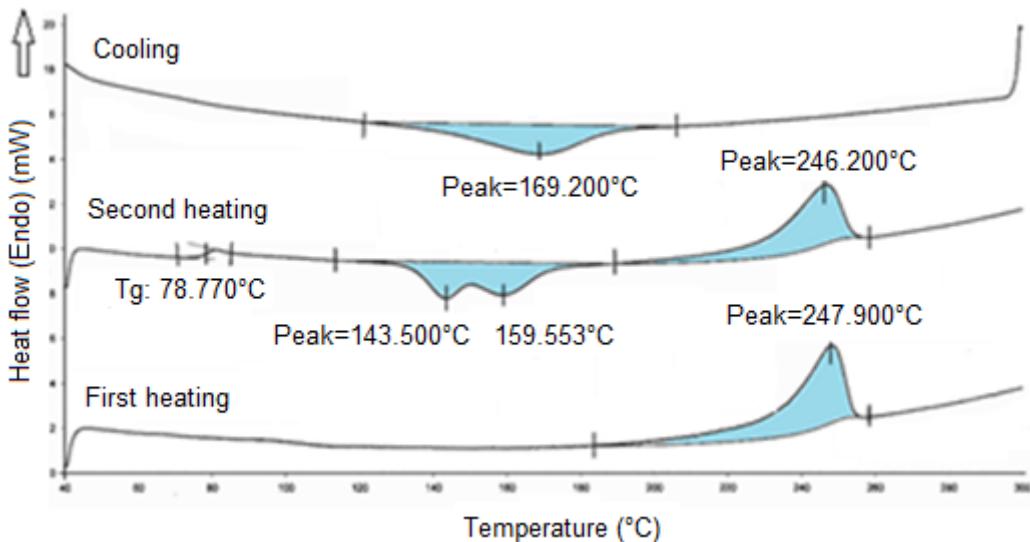


Figure 3

Differential scanning calorimetry curves of post-consumer PET

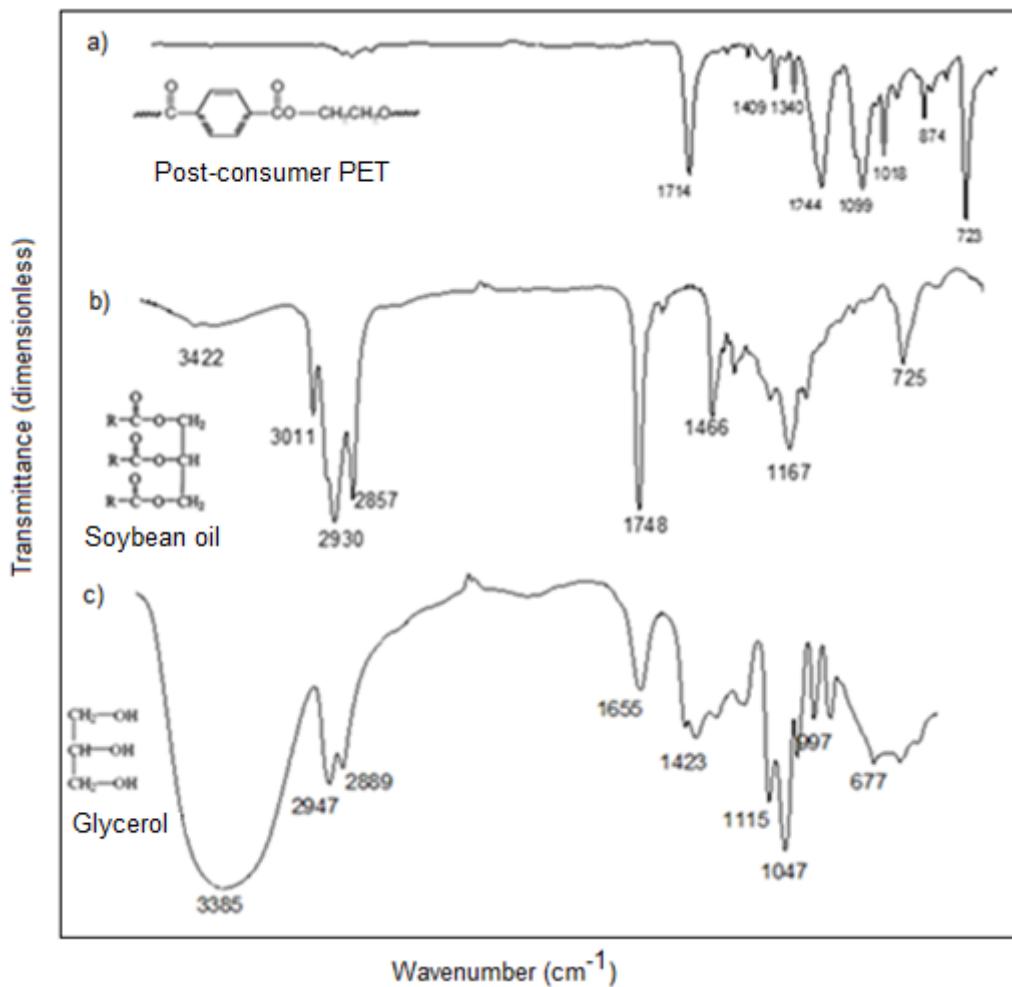


Figure 4

FTIR spectrum of a) Post-consumer PET, b) Soybean oil, c) Glycerol

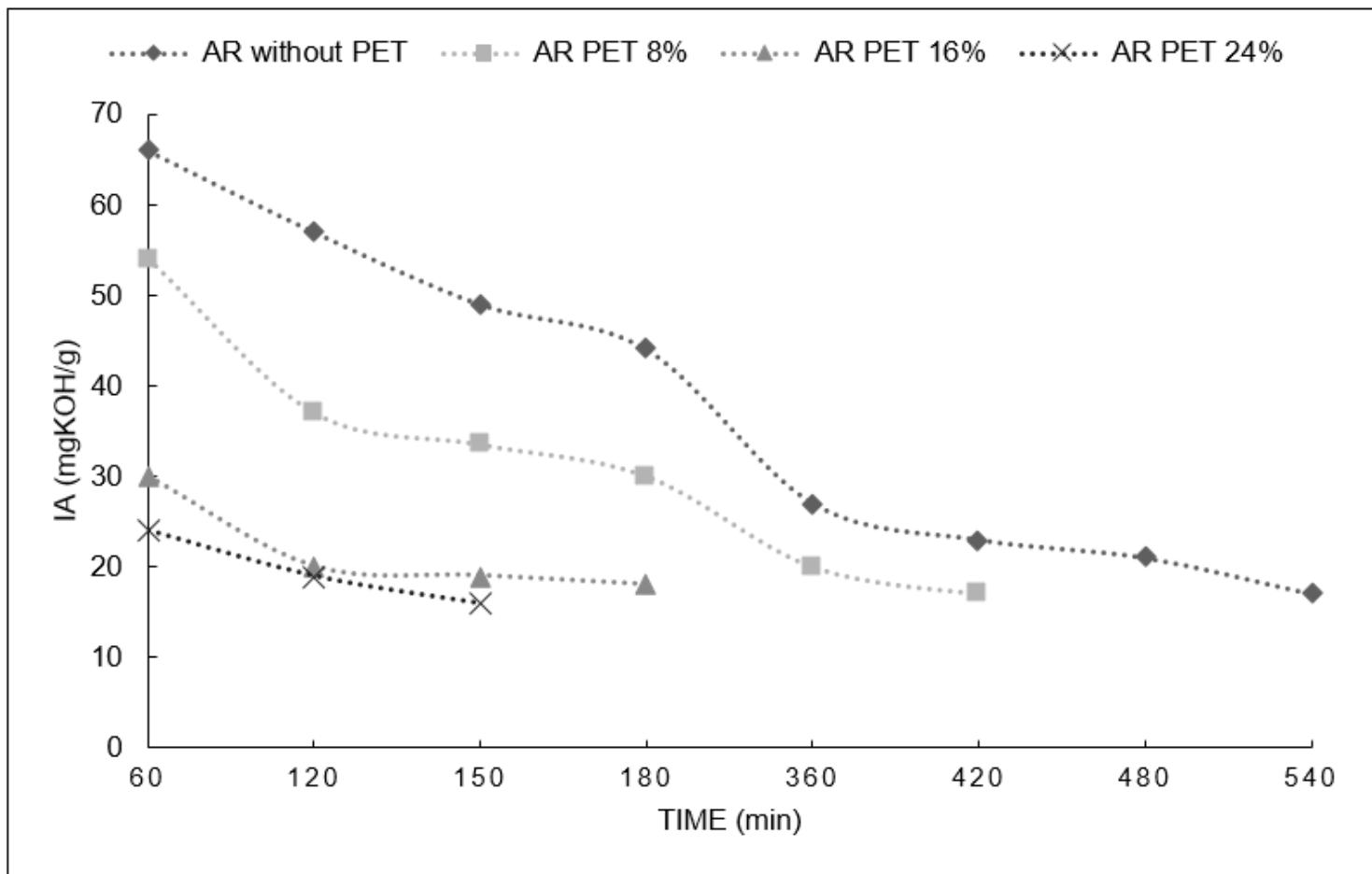


Figure 5

Esterification time versus the acidity index of the alkyl resins (AR) without PET and with 8, 16 and 24% PET.

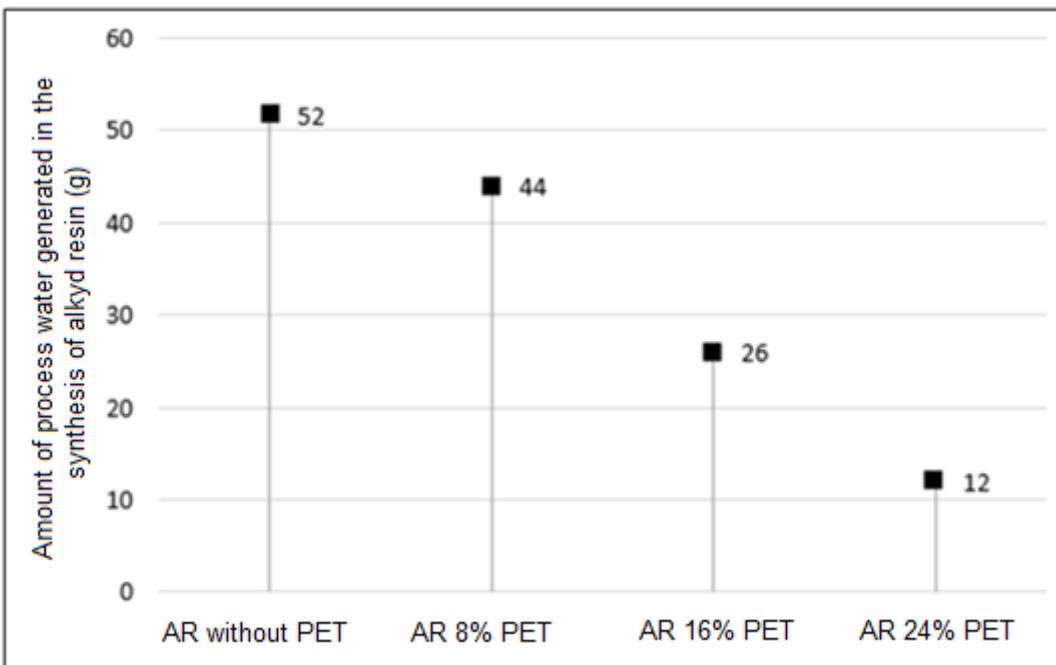


Figure 6

Amount of process water generated during the synthesis of alkyd resin.

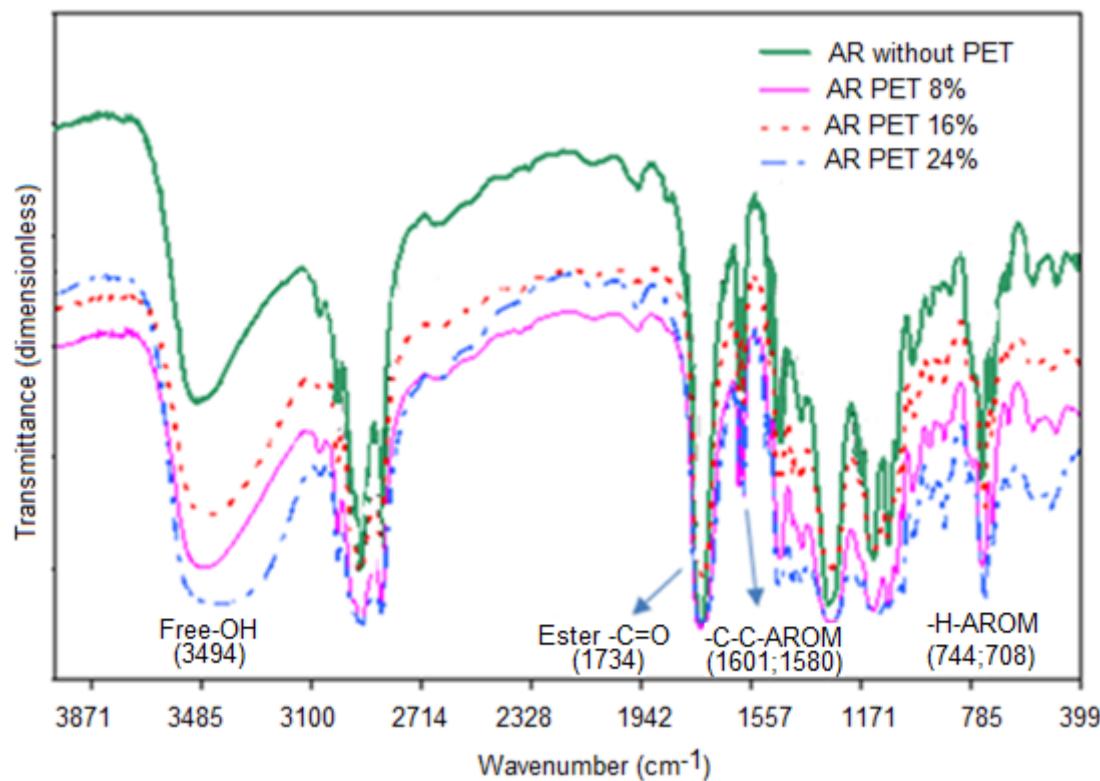


Figure 7

Spectra obtained by Fourier-transform infrared spectrometry of alkyd resins synthesized with 0, 8, 16 and 24% post-consumer PET.