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Fabrication of solvent-based alkyd paint from disposable PET water bottles: A comparative study

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ABSTRACT. This comparative study aims to prepare alternative and cheap solvent-based paint using a waste PET-based alkyd resin synthesized from waste PET intermediate, suitable for coating applications. Waste PET flakes obtained from grinding post-consumer water bottles were depolymerized by the glycolysis reaction at atmospheric pressure. The depolymerization product was extracted by hot water, and a water-soluble crystallizable fraction (WSCF) and water-insoluble fraction (WIF) were obtained. WSCF was completely used instead of the diol component in the synthesis reaction of a four-component PET-based alkyd resin that has an oil content of 60%. Besides PET-based alkyd, reference alkyd without waste PET intermediate was also synthesized. Then, solvent-based paints were prepared using PET-based alkyd, reference alkyd, and commercial alkyd as binders. Wet paint properties and physical/chemical dry film properties of paints were determined. It was observed that the viscosity, density, hiding power, and particle size values of the paint prepared with waste PET-based alkyd were in the range suitable for paint applications, and the hiding power of waste PET-based alkyd paint was better than reference and commercial alkyd paints. Glossy, relatively soft, flexible paint films with excellent adhesion strength and impact resistance, and relatively high abrasion resistance were obtained from waste PET-based alkyd paints. It was observed that the resistance of waste PET-based alkyd paint to household chemicals was better than the paint prepared with commercial alkyd, and its resistance to ethyl alcohol, vinegar, and beverages was excellent. Waste PET-based alkyd paint was less affected by solvents than commercial alkyd paint. The environmental resistance of waste PET-based alkyd paint is excellent, and the oven-cured waste PET-based alkyd paint showed excellent resistance to corrosive conditions. The use of waste PET-based alkyd resin in the paint formulation did not cause any negative effects on the wet paint, physical/chemical surface coating properties, and chemical performance tests. As a result, PET-based alkyd paints, which are prepared using waste PET-based alkyd resins synthesized from the depolymerization intermediates of PET bottles, have the same or superior coating properties compared to commercial alkyd paints. Consequently, they can be considered as a new cost-effective alternative for the paint industry.

Keywords: Poly (ethylene terephthalate), waste PET bottles, alkyd resin, solvent-based paint, coating properties, wet paint properties.

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Introduction

Today, environmental protection, sustainability, and reuse-recycling-recovery of many waste appear as crucial concepts in almost all technology fields (Höfer & Bigorra, 2007; Siyab, Tenbusch, Willis, Lowe, & Maxted, 2016; Nandy, Fortunato, & Martins, 2022). In this context, many items used in all areas of our lives are being reviewed accordingly, and efforts are made to make them less harmful to the environment during production and use as much as possible. The paints, which are among these items, are present in almost all areas of our daily lives (Van Haveren et al., 2007).

Paint is a chemical system consisting of a binder, solvent, pigment, filler, and additive. The main component of the paint is the binder and it determines the basic properties and performance of the paint. Different types of resins can be used as a binder in the production of paint, depending on the usage area and the desired properties/performance (Paiano et al., 2021).

Alkyd resins are among the frequently preferred binders in both solvent and water-based paint systems. Alkyds are oil-modified polyester resins produced by the condensation reaction of polyhydric alcohols, polybasic acids, and monobasic fatty acids (Lowell, 1984; Dullius, Ruecker, Oliveira, Ligabue, & Einloft, 2006).

The use of recycled chemicals as raw materials instead of all or part of the components used in the production of alkyd resins can also be considered a green approach, and there are various studies on this subject (Bulak & Acar, 2014; Ertaş & Güçlü, 2005; Güçlü & Orbay, 2009; Tuna, Bal, & Güçlü, 2013, Spasojevic et al., 2015; Atta, El-Ghazawy, & El-Saeed, 2013; Acar, Bal, & Güçlü, 2013; Güçlü, 2010).

In these studies, most of which were carried out by our working group, it was possible to use partially or completely waste PET depolymerization intermediates instead of the dibasic acid or diol component of the alkyd resin.

As it is known, PET is a saturated linear polyester with semi-crystalline and thermoplastic properties that has high resistance to atmospheric and environmental conditions (Acar, Durmuş, & Özgümüş, 2007; Acar, Pozan, & Özgümüş, 2008; Kasap Yeğen, Acar, & Güçlü, 2023). The recovery, recycling, and reuse of waste PET has been successfully and widely practiced for years and can be carried out effectively today (Acar, Kaşgöz, Özgümüş, & Orbay, 2006; Padhan & Sreeram, 2019; Rane et al., 2019; Ghosal & Nayak, 2022). However, the reuse-recycling-recovery processes of waste PET are not realized in the same proportion to the amount of PET consumed and the amount of waste PET thrown away as garbage. Therefore, waste PET bottles continue to be an environmental problem today.

There are a limited number of studies in the literature on paints prepared from waste PET. These studies are related to the use of glycolysis products of post-consumer PET bottles in epoxy-based paints (Bal, Ünlü, Acar, & Güçlü, 2017) and acrylic-modified water-reducible alkyd-based paints (Büyükyonga, Akgün, Acar, & Güçlü, 2020). In a different study, the aminolysis products of PET waste were used as a corrosion inhibitor ingredient in anticorrosive paints (Tawfik, Ahmed, & Eskander, 2011). In another study, the film properties of powder paints formulated with a polyester synthesized from recycled PET were investigated (Kawamura, Ito, Nishida, Yoshihara, & Numa, 2002). There is also a conference paper on recycling and, the conversion of waste PET bottles into acrylic paints (Kaliveer et al., 2020).

In the study performed by Bal et al. 2017, first, the glycolysis reaction product of waste PET was used for the synthesis of PET-based epoxy resin. Then, two epoxy-based paints were prepared using varying amounts of PET-based epoxy resin mixed with commercial epoxy resin. Wet paint properties and chemical/physical film properties of these waste PET-based epoxy paints were determined. It has been reported that the use of PET-based epoxy resin in the paint formulation does not have a negative effect on the paint properties of epoxy-based paints (Bal et al., 2017).

In another study accomplished by Büyükyonga et al. 2020, water-based paints were prepared with medium-oil acrylic-modified water-reducible alkyd resin (as a binder) which was synthesized using waste PET glycolysis product. When the wet and dry paint properties were evaluated, no difference was observed between the properties of waste PET-based and analog reference paint which did not include waste PET. Moreover, the hot water and alkali resistance of waste PET-based paint was considerably higher than the reference resin (Büyükyonga et al., 2020).

In the study executed by Tawfik et al. 2011, PET waste was subjected to an aminolysis process with ethanolamine as a degradative agent in the presence of a catalyst in sunlight. The end product bis(2-hydroxyethylene) terephthalamide was used in anticorrosive paint formulations. Thus, the weight percentages of the pigments were reduced, and compensation for these pigments was provided by the addition of waste PET degradation products (Tawfik et al., 2011).

In another study realized by Kawamura et al. 2002, the film properties of powder paints formulated with polyester synthesized from commercial recycled PET instead of ethylene glycol and terephthalic acid were investigated. In the study, the results of powder paint were comparable to those of a conventional coating (Kawamura et al., 2002).

In the study conducted by Kaliveer et al. 2020, it was reported that some of the PET waste was converted by glycolysis into viscous oil or oligomers that can be used as a binder, and the other part was converted by hydrolysis into suitable solvents. It was later stated that acrylic-based paint was formed by combining and processing these conversion products with different pigments, solvents, additives, and chemicals (Kaliveer et al., 2020).

In this study, solvent-based alkyd paints were prepared using waste PET bottles with an environmentally friendly, sustainable, and economical approach. To the best of our knowledge, an experimental and comparative study has not been reported yet on the preparation of solvent-based paint with alkyd resin including waste PET depolymerization intermediate as the diol component of four-component alkyd resin in the literature. In this respect, our study differs from other similar studies.

In the scope of this study, the depolymerization intermediates of post-consumer PET water bottles were completely used instead of the diol component of alkyd resins to be used as binders in paint formulations. Then, the production of solvent-based alkyd paint from waste PET was successfully achieved by using this synthesized waste PET-based alkyd resin. Both wet paint properties and coating (dry paint film) properties of the prepared waste PET-based paint were compared with the reference paint prepared in the same way but without the waste PET intermediate and with the commercial alkyd-based paint.

Experimental

Material and Instruments

In the glycolysis reactions, waste poly (ethylene terephthalate) (PET) flakes (4-8 mesh) obtained from post-consumer water bottles and ethylene glycol (EG) were used. The tall oil fatty acid (TOFA) (SYLFAT 2, iodine index 155, acid index 195 mg KOH g^{-1}) used in the synthesis of alkyd resins is the product of Arizona Chemical (Kraton Company) (USA). Other chemicals were purchased from Sigma-Aldrich (USA) and Merck (Germany). The bentone used in paint formulations was supplied from Boysan Boya (Turkey). The dispersion and wetting agent for solvent-based paint systems (DISPERBYK-2151) was supplied from BYK (Germany). Titanium dioxide (TiO_2), butyl glycol, and soy lecithin were purchased by Sigma Aldrich. The colored pigment (Eisenoxydrot 190 F) is a Bayer product (Germany). Cobalt, zirconium, manganese, and calcium naphthenate used as a drier were supplied from Akpa Kimya (Turkey). All other materials are of analytical or synthesis purity.

Methods

A high-speed disperser (Yökeş brand VBR-12 model, Turkey) was used in the preparation of the waste PET-based alkyd paints. In wet paint tests, Brookfield RVT rotary viscometer (Brookfield Engineering, USA) and BYK-Gardner Instruments (BYK, Germany) products such as steel density cup, steel flow cup (DIN cup), steel grindometer, and hiding power/opacity test card (Byko-chart) were used. The physical coating properties of the dry paint films were tested by a Drying Time Tester (Erichsen, 415/E model, Germany), Pendulum Hardness Tester (Sheen, König model, UK), Cross-Cut Adhesion Tester (Erichsen, GS 10 model, Germany), Falling Sand Abrasion Tester (Erichsen, 2511-11 model, Germany), Impact Tester (BYK Gardner, PF-1115 Light-Duty model, Germany) and Gloss meter (Sheen, 101 N mini model, single angle, 60º, UK). The corrosion resistance of paint films (salt spray test) was determined using the Salt Fog Corrosion Test Chamber (VLM, CCT 600-TL model, Germany).

Synthesis of waste PET-based alkyd resin as a binder

Step 1: Waste PET depolymerization

The depolymerization of waste PET by glycolysis with ethylene glycol (EG) was carried out in the presence of excess EG, at atmospheric pressure, at high temperature, and with zinc acetate (ZnAc) catalysis. The five-neck glass reactor system equipped with a mechanical stirrer, thermometer, gas-bubbler, and reflux-condenser was used as the reaction system heated by a heating mantle. In this reaction, the mole ratio of PET/EG was 1/6. After the waste PET, EG, and ZnAc (as a catalyst, 1% by wt. of PET) were loaded into the reactor, the reaction temperature of 180-190°C was reached in about 1h in a nitrogen atmosphere with continuous stirring (280 rpm). The reaction was continued for 6h at this temperature. The depolymerization reaction (glycolysis) conditions of waste PET with EG are summarized in Table 1.

Table 1. The depolymerization conditions of waste PET.

PET/EG molar ratio	Catalyst (ZnAc)	Temperature (°C)	Pressure	Time (h)
1/6	1% by weight of PET	180-190	Atmospheric pressure	6

The raw depolymerization product obtained at the end of this reaction was fractionated with boiling water by extraction and purified (excess glycol was removed). Thus, firstly, a water-insoluble fraction (WIF) was obtained. Then, a water-soluble crystallizable fraction (WSCF) was obtained by cooling to 4°C and filtration. The WIF and WSCF were dried under vacuum at 40°C. These intermediates were characterized by acid value (AV) and hydroxyl value (HV) analyses and Differential Scanning Calorimeter (DSC) analysis using Linseis DSC-PT10 device (Germany). AV was determined by acid-base titration (ASTM D-1639). HV was determined by acetylation of samples dissolved in acetylation reagent (pyridine/acetic anhydride: 127 mL 1000 mL^{-1}) (back-titration method) (ASTM E-222). The characterization methods used for waste PET intermediates are summarized in Table 2.

Table 2. Characterization methods used for waste PET intermediates.

Characterization	Standard	Method	Requirements
Acid value analysis	ASTM D-1639	Volumetric	0.1 N KOH with methanol
Hydroxyl value analysis	ASTM E-222	Volumetric	Acetylation reagent, 1 N NaOH
DSC analysis	-	Calorimetric	DSC device (Linseis DSC-PT10)

Step 2: Waste PET-based and reference alkyd resin synthesis

At this stage, long oil alkyd resins (60% oil content) were prepared using the fatty acid method. Alkyd resin synthesis reactions were carried out in a five-necked glass reactor system containing a mechanical stirrer, reflux-condenser + Dean-Stark part, gas bubbler, and thermometer. Reactions were monitored by periodic acid value determinations. The reactions were terminated as soon as the desired acid value was reached. Using this system, two four-component alkyd resins were synthesized: "waste PET-based alkyd resin" and "reference alkyd resin". Tall oil fatty acid (TOFA), phthalic anhydride (PA), pentaerythritol (PE), and ethylene glycol (EG) were used to synthesize "reference alkyd resin". For the synthesis of "waste PET-based alkyd resin"; TOFA, PA, PE, and waste PET depolymerization intermediate (WSCF) (instead of EG) were used. In the preparation of alkyd resin formulations, the "K alkyd constant" system (Patton, 1962) was used (K = 1.05 and R = 1.15). (K constant is "total amount of moles/acid equivalent", and the R-value is "base equivalent/acid equivalent").

During alkyd resin synthesis, potassium hydroxide dissolved in methanol (1% by weight of the total amount) as a catalyst and xylene (10% by weight of the total amount) as a solvent were added to the reaction medium. The synthesis reactions were continued for approximately 6h at 210-220°C until the desired acid value was reached. Symbols and synthesis reaction conditions of alkyd resins are presented in Table 3.

Table 3. Symbols and synthesis reaction conditions of alkyd resins.

Alkyd resin	Symbol	Components				Oil-length (%)
		Glycol	Diacid	Polyol	Fatty acid	
Reference alkyd	REF-ALK	EG	PA	PE	TOFA	60
Waste PET-based alkyd	PET-ALK	WSCF	PA	PE	TOFA	60

WSCF: water-soluble crystallizable fraction

Paint production using waste PET-based alkyd resin

At this stage, three paints were prepared by using "waste PET-based alkyd resin", waste PET-free "reference alkyd resin", and "commercial alkyd resin" as a binder in synthetic paint formulations.

For the preparation of these solvent-based paints, "pigment paste" was prepared in the first step. To prepare the pigment paste, alkyd resin, wetting agent, bentone, pigment, and titanium dioxide were loaded into the mixing chamber of the disperser. Subsequently, this mixture was first mixed at 5000 rpm for 5 min. (peripheral speed 10 m s^{-1}) and 10 min. at 10000 rpm (peripheral speed 20 m s^{-1}). A completely homogeneous mixture was achieved at this speed. Table 4 shows the composition of the prepared pigment paste.

Table 4. Composition of pigment paste.

Component	Ratio, %
Alkyd resin (binder)	71.28
Titanium dioxide (white pigment/filler)	14.26
Colored pigment (Eisenoxydrot 190 F)	14.26
Bentone (anti-slump, thickener, and thixotropic agent)	0.18
Disperbyk-2151 (wetting/dispersing agent)	0.02

In the second stage, prepared pigment paste, alkyd resin, and other components in the formulation were loaded into the mixing chamber of the disperser. Subsequently, this mixture was mixed at 6000 rpm (peripheral speed 12 m s^{-1}) for 15 min. and at 9500 rpm (peripheral speed 20 m s^{-1}) for 30 min. A complete dispersion was achieved at this speed. After the addition of Zr, Co, Mn, and Ca based driers, the disperser was mixed for another 15 min. at the same speed (9500 rpm). At this stage, for comparison, a solvent-based paint was also prepared using a commercial alkyd resin with similar properties besides those prepared with PET-based and reference alkyds.

Table 5 shows the formulations of the solvent-based paints prepared using waste PET-based alkyd resin (containing PET intermediate), reference alkyd resin (without PET intermediate), and commercial alkyd resin (with similar properties and supplied from the market) as a binder.

Table 5. Formulations of solvent-based paints prepared using waste PET-based, reference and commercial alkyd resin.

Components of solvent-based paints	Ratio, %
Binder (alkyd resin) (diluted to 70% with white spirit)	77.15
Pigment paste	18.33
Butyl glycol (viscosity and flow improver additive)	1.83
Zinc phosphate (anticorrosive additive)	0.74
Soy lecithin (auxiliary agent for wetting/dispersing, stabilizer)	0.39
Bentone (rheological additive)	0.22
Disperbyk-2151 (wetting/dispersing agent)	0.22
Driers (Co, Mn, Zr, Ca based driers)	1.12

The ratios (%) of mixture of the driers used in paint formulations are also presented in Table 6.

Table 6. Driers ratios in paint formulations.

Drier	Ratio, %
Cobalt naphthenate (6% solution) (primary drier)	24.8
Manganese naphthenate (6% solution) (primary drier)	12.8
Zirconium naphthenate (6% solution) (auxiliary or secondary drier)	37.6
Calcium naphthenate (6% solution) (auxiliary or secondary drier)	24.8

After preparation of the paints, they were diluted to 70% solids content using white spirit.

Wet paint properties

Viscosity (ASTM D 2196), flow time (ISO 2431), density (ISO 2811), hiding power (ISO 6504), and particle size (ASTM D 1210-05) of paints prepared with waste PET-based, reference, and commercial alkyds were determined according to standards by wet paint tests. These tests are summarized together in Table 7.

Table 7. Wet paint tests.

Wet paint test	Standard	Equipment
Dynamic viscosity	ASTM D 2196	Brookfield Rotational Viscometer (Brookfield Engineering)
Flow-time (kinematic viscosity)	ISO 2431	Steel Flow-Cup (DIN-Cup) (BYK)
Density	ISO 2811	Steel Density-Cup (BYK)
Hiding power	ISO 6504	Hiding Power/Opacity Test Card (Byko-Chart) (BYK)
Pigment particle size	ASTM D 1210-05	Steel Grindometer (Hegman Gauge) (BYK)

Dry paint film properties

To test the coating properties of paints produced using waste PET-based, reference, and commercial alkyds, paint films were prepared using a 50µ applicator (BYK) on different surfaces (glass and metal plates) according to the test method. The prepared paint films were dried under room conditions for 72h. Additionally, the other paint film series were kept at room conditions for 72h, and then they were oven-cured at 110°C for 1h. Thus, air-dried (AD) and oven-cured (OC) films were obtained. Subsequently, physical surface coating tests, chemical surface coating tests (resistance to household chemicals), and chemical performance tests (solvent resistance, environmental resistance, corrosion resistance) were applied to all films.

Physical surface coating tests

Drying degree (drying time) (DIN 53150), hardness (DIN 53157), adhesion strength (ASTM D 3359-76), abrasion resistance (ASTM D 968-05), impact resistance (ASTM D 2794-69) and gloss (ASTM D 523) of paint films prepared from waste PET-based, reference and commercial alkyd were determined according to standards by dry paint tests. These tests are summarized together in Table 8.

Table 8. Physical surface coating tests.

Test	Standard	Equipment
Drying Degree	DIN 53150	Drying Degree Tester (Erichsen, 415/E)
Hardness	DIN 53157	Pendulum Hardness Tester (Sheen König Pendulum)
Adhesion Strength	ASTM D 3359-76	Cross-Cut Tester (Erichsen, GS 10)
Abrasion Resistance	ASTM D 968-05	Falling Sand Abrasion Tester (Erichsen, 2511-11)
Impact Resistance	ASTM D 2794-69	Impact Strength Tester (BYK-Gardner, PF-1115 Light-Duty)
Gloss	ASTM D 523	Gloss meter (Sheen, 101 N, mini, single angle) (°60)

Brief explanations of these tests are given below.

Drying Degree: In this test (Modified Bandow-Wolff method), there are 7 drying stages (or degrees), and the maximum drying stage is 7. The drying degree is estimated by the adherence or non-adherence of typewriter paper disks or glass beads to the film. In stage 1, glass beads are used. Poured glass beads to the film are allowed to stay on the surface for 10 s. In the remaining stages, paper disks are used, and the drying stage is determined by applying load (range from 5 to 5000 g cm^{-2}) for 60 s.

Hardness: This test is based on the measurement of the damping of a pendulum oscillating on the paint film. The pendulum pivots on two ball faces of 5 mm diameter rest on the surface of the film under test. The damping time of the König pendulum on a standard glass test surface within the specified limits of amplitude (from 6° down to 3°) is 250±10 secs. which corresponds to between 172 and 185 complete oscillations (Sheen Instruments, 2010).

Adhesion Strength: In this test method, the film on the glass plate is scratched transversely and longitudinally with a 6-blade cross-cut cutter, creating a lattice pattern and comparing the image of this pattern with the standard. A value of 100% corresponds to excellent adhesion strength.

Abrasion Resistance: In this test, hard sand is dropped down via a vertical tube onto a film-coated panel located at a 45° angle, and the amount of sand (mL) which required to remove a certain thickness of the coating was determined.

Impact Resistance: In this test, different steel cylindrical weights (1 and 2 kg) are dropped by a guide tube onto the film on a metal panel from changing heights. Deformation caused by the falling weight is observed as cracking or peeling. The result is determined in kg x cm, depending on the weight and the drop height at which the deformation occurs.

Gloss: This test method is based on the principle of sending light at a certain angle to the film surface on the glass plate and measuring the specular (mirror-like) reflectance of light. Before measurements, the device is calibrated with a standard black glass. The result is given as a gloss unit (GU).

Chemical surface coating tests

In the scope of the household chemicals resistance test (ASTM D 1308), the effects of various chemicals such as hot and cold distilled water, alkali, acid, soap, detergent, ethyl alcohol, acetic acid (vinegar), and beverages (tea, coffee, cola) on paint films were determined. These tests are summarized together in Table 9.

Table 9. Chemical surface coating tests (household chemicals resistance tests).

Test	Standard	Test Solution/Method
Water resistance	ASTM D 1308	Cold distilled water (20°C) / immersion method Hot distilled water (80°C) / immersion method
Alkali resistance	ASTM D 1308	NaOH (0.3% wt.) / immersion method
Acid resistance	ASTM D 1308	H_2SO_4 (3% wt.) / immersion method
Soap resistance	ASTM D 1308	Liquid yellow soft soap (KOH-based Arab soap) solution (8 g L^{-1}) / immersion method
Detergent resistance	ASTM D 1308	Dish detergent solution (5 g L^{-1}) / immersion method
Ethyl alcohol resistance	ASTM D 1308	Ethyl alcohol (50% v.) / spot test method
Acetic acid (vinegar) resistance	ASTM D 1308	Acetic acid (3% wt.) / spot test method
Beverage resistance (Tea, Coffee, Cola)	ASTM D 1308	Tea: 1 tea bag in 100 mL boiled water (It was brewed for 5 min.) / spot test method Coffee: 2.5 g coffee in 100 mL boiled water / spot test method Cola: Any cola brand was chosen / spot test method

Immersion method: The film-coated glass plate was immersed in the solution and observed for 48h; Spot test method: After dropping (1 mL) the solutions/beverages onto the paint film on a glass plate, the plate was covered with a petri dish. The film surface was observed by wiping the drops at certain intervals for 4h.

Chemical performance tests

In the scope of chemical performance tests, the solvent resistance (ISO 2812-3, Mizutani et al., 2006), environmental resistance (Mizutani, Arai, Miyamoto, & Kimura, 2006), and corrosion resistance (DIN EN ISO 9227) of the paint films were determined. These tests are summarized together in Table 10.

Table 10. Chemical performance tests.

Test	Reference/Standard	Test Solution/Method
Solvent resistance	ISO 2812-3 Mizutani et al., 2006	Methanol, Toluene, Ethyl Acetate, Acetone A piece of gauze (1 x 1 cm) is dipped into the solvent. After removing the excess solvent, it is placed on the film surface and covered with a petri dish. It is waited 30 min. at room temp.
Environmental resistance (wet, cold dry and heat cycle)	Mizutani et al., 2006	The paint film on the glass plate is kept in distilled water at room temp. for 18h. Then, it is kept in the deep freezer at -20±2°C for 3h. After that, it is kept in the oven at +50±2°C for 3h. At the end of all these stages, 1 cycle is completed. These processes were repeated 10 times.
Corrosion resistance (salt spray test)	DIN EN ISO 9227	In the salt-fog corrosion test chamber at 35±2°C, NaCl solution (5% wt.) is sprayed continuously on the coating for the desired test period.

Results and discussion

Glycolysis reaction of waste PET

The percentage ratios (yield %) of depolymerization intermediates obtained from the glycolysis reaction of waste PET with EG and the acid value (AI) and hydroxyl value (HI) results of these are presented in Table 11.

Table 11. The properties of depolymerization intermediates.

Intermediate	Yield, % (wt.)	Acid value (mg KOH g^{-1})	Hydroxyl value (mg KOH g^{-1})
WSCF	86.5	< 2	445
WIF	13.5	< 2	250

As seen in Table 11, as a result of the depolymerization reaction of waste PET, 86.5% WSCF and 13.5% WIF were obtained. The hydroxyl values of the WSCF and WIF were found to be 445 and 250 mg KOH g^{-1}, respectively. According to the literature, the hydroxyl values of PET's hydroxyl-terminated monomer, bis (2-hydroxyethyl terephthalate) (BHET), and its dimer are 442 and 250 mg KOH g^{-1}, respectively (Chen, 2003).

DSC curves of the WSCF and WIF obtained at the end of the depolymerization reaction are also presented in Figures 1 and 2.

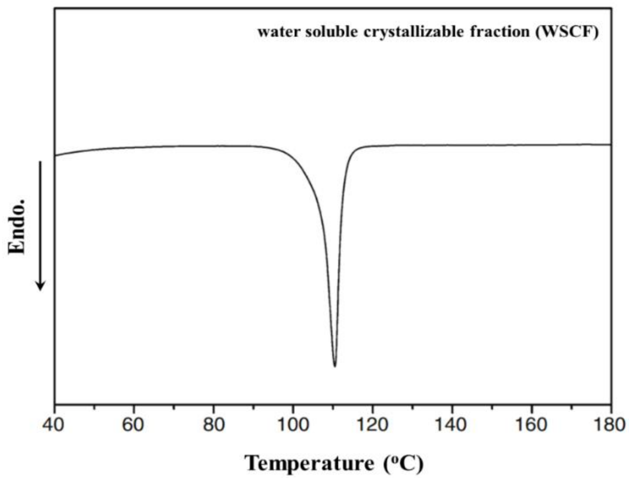

Figure 1. DSC curve of WSCF.

The melting points of both intermediates were determined with DSC analysis made in a nitrogen atmosphere with approximately 20 mg samples on the Linsesis DSC-PT10 DSC device by heating from room temperature to 350°C at a heating rate of 10°C min.$^{-1}$. As seen from the DSC curves, there are sharp melting peaks in the WSCF curve at 110°C, and in the WIF curve at 173°C. According to the literature, the melting point of the hydroxyl-terminated monomer of PET (BHET) is 109-110°C, and the hydroxyl-terminated dimer of PET is 173-174°C (Brandrup & Immergut, 1966).

When all these results are evaluated together, it can be seen that hydroxyl-terminated oligomers of PET are obtained as a result of the glycolysis reaction of waste PET at atmospheric pressure and EG excess. Here, the WSCF obtained at a ratio of 86.5% is the hydroxyl-terminated monomer (BHET) of PET, and the WIF obtained at a ratio of 13.5% is the hydroxyl-terminated dimer of PET. The obtained BHET was used instead of

EG as the diol component in the waste PET-based alkyd resin synthesis reaction. Then, prepared waste PET-based alkyd resin was used as a binder for a solvent-based paint system.

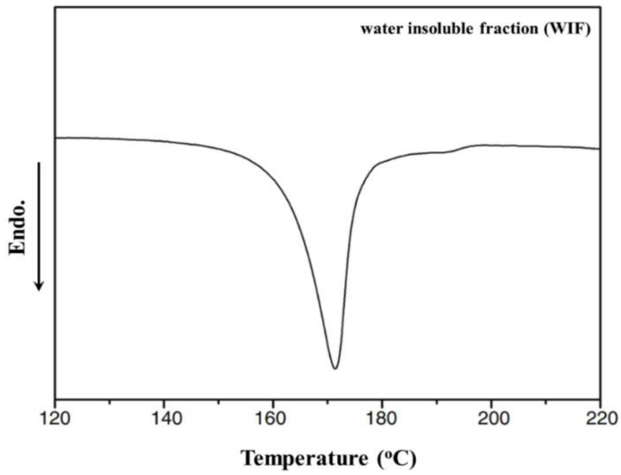

Figure 2. DSC curve of WIF.

Wet paint properties

The results of wet paint tests (at 22-23°C) of all prepared paints are presented in Table 12.

Table 12. Wet paint test results of solvent-based paints.

Wet paint properties	Waste PET-based alkyd paint (PET-paint)	Reference alkyd paint (REF-paint)	Commercial alkyd paint (COM-paint)
Dynamic viscosity (cP)	1800	3040	21600
Flow-time (kinematic viscosity) (sec)	86 (DIN Cup 6) 43 (DIN Cup 8)	156 (DIN Cup 6) 71 (DIN Cup 8)	- 375 (DIN Cup 8)
Density (g cm^{-3})	0.9910	0.9984	0.9726
Hiding power (g cm^{-2}) Hiding power (m^2 kg^{-1})	0.0203 4.9730	0.0212 4.7179	0.0232 4.4955
Pigment particle size (grinding fineness) (micron, μ)	12.5	17.5	17.5
Pigment particle size (grinding fineness) (Hegman, NS)	7	6.75	6.5

As seen in Table 12, the densities of waste PET-based alkyd (PET-paint) and reference alkyd (REF-paint) paints are very close to each other and are higher than commercial alkyd-based paint (COM-paint). In addition, the viscosity and flow time values of PET-based alkyd paint prepared with waste PET intermediate (1800 cP, 43 sec) are lower than reference paint (3040 cP, 71 sec) and commercial paint (21600 cP, 375 sec). These values are compatible with the viscosity values of alkyds synthesized in previous studies, and the viscosity can vary depending on the length of the molecular chain or molecular weight of the waste PET intermediate used in resin synthesis (Büyükyonga et al., 2020; Bal et al., 2017). In order to obtain the desired viscosity value, it is also possible to change the binder resin ratio used in the paint composition.

Here, the paints were obtained as stable dispersions, and the pigment particle size (grinding fineness) of all three paints, determined using a grindometer, was obtained around 6.5-7 NS. Widely used in the paint industry dimensionless Hegman unit (or National Standard unit, NS) are defined in terms of an inverted size scale of mil or micrometer (1 NS = 4 mil = 101.6 μ; 4 NS = 2 mil = 50.8 μ; 6 NS = 1 mil = 25.4 μ; 8 NS = 0 mil = 0 μ) (Doubleday & Barkman, 1950).

As known, it is important to determine the grinding fineness of paint. The pigment in a paint determines its optical properties, flow properties (rheology), durability, opacity, gloss, and storage stability (Lambourne, & Strivens, 1999; Tadros, 2013). Color development (i.e. tinting strength), gloss, hiding power, opacity, surface appearance, and aesthetics are paint and ink parameters that are inversely proportional to grind fineness. A pigment with a larger particle size has less tint or color strength (Gueli, Bonfiglio, Pasquale, & Troja, 2017). Insufficient grinding degree of pigment changes the color uniformity, brightness, and opacity of the paint. That is, the hiding power of the paint becomes low, and the color intensity and brightness of the pigment decreases (McGonigle & Ciullo, 1996). As poorly ground large pigment particles break down over time, they may change the color of the paint in the paint package. At the same time, paints with an insufficient grinding degree of the pigment have also low resistance to atmospheric effects (moisture, sunlight, etc.) and chemicals, which is an undesirable situation (Lambourne, & Strivens, 1999; Tadros, 2013).

Herein, the pigment particle size (12.5 μ) of PET-based alkyd paint is at the desired level for paint formulations, and it is lower than commercial paint (17.5 μ). The hiding power value is determined as 0.0203 g cm^{-2}, or in other units, 4.9730 m^2 kg^{-1} for waste PET-based alkyd paint. This means that when waste PET-based alkyd paint is used, the amount of paint covering of 1 m^2 area is 0.2 kg, or 1 kg of paint covers 4.97 m^2 area. Compared to reference and commercial alkyd paints, it is seen that the hiding power ability of waste PET-based alkyd paint is better.

When the wet paint test results are evaluated together, the use of waste PET-based alkyd resin did not have a negative effect on the wet paint properties of the synthetic paint. On the contrary, more fluid paint having lower viscosity with more hiding power was prepared using waste PET-based alkyd.

Dry paint film properties

Physical surface coating properties

First, physical surface coating tests such as drying degree, hardness, adhesion strength, abrasion resistance, impact resistance, and gloss were applied to the paint films. The results of all physical surface coating tests applied to dry paint film are presented in Table 13.

Table 13. Physical surface coating test results of solvent-based paints.

Test	Drying method	PET-paint	REF-paint	COM-paint
Drying Degree	Air-dried at room temp. for 24h	4. stage	4. stage	4. stage
	Air-dried at room temp. for 48h	6. stage	6. stage	6. stage
	Air-dried at room temp. for 72h	6. stage	6. stage	6. stage
	Oven-cured at 110°C for 1h	7. stage	7. stage	7. stage
Pendulum Hardness (König second)	Air-dried	17	24	17
	Oven-cured	32	50	35
Adhesion Strength (%)	Air-dried	100	100	100
	Oven-cured	100	100	100
Abrasion Resistance (mL sand)	Air-dried	4000	4500	4500
	Oven-cured	3500	2250	2250
Impact Resistance (kg x cm)	Air-dried	> 200	> 200	> 200
	Oven-cured	> 200	> 200	> 200
Gloss at °60 (GU, gloss unit)	Air-dried	89	90	90
	Oven-cured	87	86	90

Air-dried (72h, at room temp.) Oven-cured (1h, at 110°C).

As seen in Table 13, all paint films reached the 6th drying degree after 48h and remained at the 6th drying degree after 72h at room temperature in air. This drying degree probably corresponds to the hard-dry stage according to the Finger-Touch method (ASTM D1640). Following the curing at 110°C for 1h, all paint films reached the 7th drying degree (through-dry), which is the highest drying degree.

The adhesion of all paint films is excellent and 100%. Similarly, their impact resistance is excellent. Paint films did not show any difference in terms of impact resistance, adhesion, and gloss properties.

Otherwise, hardness and abrasion resistance properties vary slightly, but they are very close to each other. As known, the oscillation time (or damping time) of a standard glass plate (the hardest material according to this standard) is 250 König seconds (Balcı & Iyim, 2014). In addition, according to the standards, values higher than 85 GU obtained in gloss measurements at 60° correspond to very glossy coatings (Sönmez, 2020). According to these, it is seen that all paint films are very glossy and relatively soft. It is also seen that the hardness values are slightly improved by oven-curing in all paint films. Conversely, the decrease in abrasion resistance values was observed with oven-curing.

When physical surface coating properties are evaluated together, it has been observed that flexible paint films that are glossy, relatively soft, have excellent adhesion and impact resistance, and have relatively high abrasion resistance are obtained from waste PET-based, reference, and commercial alkyd paints. It has been concluded that the use of alkyd resin synthesized with waste PET glycolysis intermediate in paint formulation does not cause any negative effects.

Chemical surface coating properties

Chemical resistance tests (household chemicals resistance tests) such as cold and hot water, acid, detergent, alkali, soap, ethyl alcohol, acetic acid (vinegar), and beverage (tea, coffee, cola) resistance were applied to the paint films. The results obtained are presented sequentially under the headings below.

Household chemicals resistance of paint films (immersion method)

The results of tests performed by the immersion method (in the scope of household chemicals resistance tests applied to dry paint film) are presented in Table 14.

In the immersion tests conducted according to ASTM D 1308-02 standard, the film-coated glass plate was immersed in the related solution for 48h, and the effects on the film surface were observed (as summarized in Table 9).

As seen in Table 14, air-dried and oven-cured films prepared from waste PET-based and reference alkyd paints showed excellent cold water, acid, and detergent resistance. However, a slight effect from hot water was observed in air-dried films prepared from waste PET-based and reference alkyd paint. In contrast, an improvement in hot water resistance was achieved by oven curing of these films, and only small bubbles appeared in paint films.

In the alkali resistance test, roughness was observed on the film surface after 24h in air-dried waste PET-based and reference alkyd paint films. However, an improvement in the alkali resistance of these paint films was acquired with oven curing. Thus, only minor changes (lightening in color in the oven-cured reference alkyd paint film, and a slight wrinkling on the surface in the oven-cured waste PET-based alkyd paint film) were observed after 24h. On the other hand, at the end of 48h, both air-dried and oven-cured waste PET-based alkyd paint films were affected and separated from the substrate. Similarly, the paint film prepared with commercial alkyd was also affected by the alkali solution, and the air-dried paint film completely dissolved after 48h.

Table 14. The results of tests performed by immersion method within the scope of household chemicals resistance.

Test solution	Drying method	Time	PET-paint	REF-paint	COM-paint
Cold distilled water (20°C)	Air-dried	24h	No effect	No effect	Color lightened
		48h	No effect	No effect	Color lightened
	Oven-cured	24h	No effect	No effect	Color lightened
		48h	No effect	No effect	Color lightened
Acid solution H_2SO_4 (3% wt.)	Air-dried	24h	No effect	No effect	Color lightened
		48h	No effect	No effect	Color lightened
	Oven-cured	24h	No effect	No effect	Color lightened
		48h	No effect	No effect	Color lightened
Detergent solution (5 g L^{-1})	Air-dried	24h	No effect	No effect	Color lightened
		48h	No effect	No effect	Color lightened
	Oven-cured	24h	No effect	No effect	Color lightened
		48h	No effect	No effect	Color lightened
Hot distilled water (80°C)	Air-dried	24h	Roughness	Roughness	Bubble formation
		48h	Slight discoloration	Slight discoloration	Bubble formation
	Oven-cured	24h	Bubble formation	Bubble formation	Bubble formation
		48h	Bubble formation	Bubble formation	Bubble formation
Alkali solution NaOH (0.3% wt.)	Air-dried	24h	Roughness	Roughness	Color lightened
		48h	Film left the surface	Roughness	Dissolution
	Oven-cured	24h	Wrinkle	Color lightened	Color lightened
		48h	Film left the surface	Color lightened	Color lightened
Soap solution (8 g L^{-1})	Air-dried	24h	Wrinkle	Color lightened	Color lightened
		48h	Film left the surface	Wrinkle	Color lightened
	Oven-cured	24h	Color lightened	Color lightened	Color lightened
		48h	Color lightened	Color lightened	Color lightened

Air-dried (72h, at room temp.) Oven-cured (1h, at 110°C)

In the soap resistance test, while effects such as color lightening and wrinkling were observed in the air-dried waste PET-based and reference alkyd paint films after 24h, waste PET-based alkyd paint film left the surface of the substrate after 48h. A significant improvement occurred in the soap resistance of these paint films with oven curing. At the end of 48h, only the colors of the oven-cured waste PET-based and reference alkyd paint films had lightened.

It is known that alkyd resins have poor resistance to alkali due to hydrolysable ester bonds (Saravari & Praditvatanakit, 2013). However, waste PET-based alkyd paints were able to resist alkali solution (NaOH) and KOH-based basic soap solution for up to 48h. This result indicates that this feature can be further improved.

When the results of the household chemical resistance test (performed by immersion method) are evaluated together, it is seen that the resistance of waste PET-based and reference alkyd paints to household chemicals is better than that of the paint prepared with commercial alkyd. While the paint film prepared with commercial alkyd is slightly affected by all test solutions, the cold water, acid, and detergent resistances of waste PET-based and reference alkyd paint are excellent. In addition, the properties of these films (which are slightly affected by hot water and resistant to alkali and soap solutions for 24h but are affected after 48h) had also been slightly improved by curing.

Household chemicals resistance of paint films (spot test method)

The results of tests performed by the spot test method (in the scope of household chemicals resistance tests applied to dry paint film) are presented in Table 15.

In the spot tests conducted according to ASTM D 1308-02 standard, 50% ethyl alcohol solution, vinegar (3% acetic acid solution), tea, coffee, and cola were dropped on the paint film and kept for 4h, and the effects on the film surface were observed (as summarized in Table 9).

As seen in Table 15, the air-dried and oven-cured waste PET-based, reference, and commercial alkyd paint films were not affected by any of these household chemicals after 4h. All paint films have excellent ethyl alcohol, vinegar, and beverage resistance.

Table 15. The results of tests performed by spot test method within the scope of household chemicals resistance.

Test solution		Drying method	Time	PET-paint	REF-paint	COM-paint
Ethyl alcohol (50% v.)		Air-dried	4h	No effect	No effect	No effect
		Oven-cured	4h	No effect	No effect	No effect
Acetic acid (3% wt.) (Vinegar)		Air-dried	4h	No effect	No effect	No effect
		Oven-cured	4h	No effect	No effect	No effect
Beverage	Tea	Air-dried	4h	No effect	No effect	No effect
		Oven-cured	4h	No effect	No effect	No effect
	Coffe	Air-dried	4h	No effect	No effect	No effect
		Oven-cured	4h	No effect	No effect	No effect
	Cola	Air-dried	4h	No effect	No effect	No effect
		Oven-cured	4h	No effect	No effect	No effect

Air-dried (72h, at room temp.) Oven-cured (1h, at 110°C).

Solvent resistance and environmental resistance of paint films

The results of solvent resistance and environmental resistance tests of paint films are presented in Table 16.

The gauze pieces (1x1 cm) immersed in methanol, toluene, ethyl acetate, and acetone were kept on the surface of the paint films for 30 min. at room temperature, and the changes on the film surface were observed (as summarized in Table 10). This standard method (ISO 2812-3), which uses an absorbent medium for determining the resistance of the coating to the effects of solvents/liquids, enables one to determine the effects of the test substance on the coating, and can also assess the damage to the substrate if necessary.

Table 16. The results of solvent resistance and environmental resistance tests.

Test		Drying method	Time	PET-paint	REF-paint	COM-paint
Environmental resistance	Wet-cold dry-heat cycle	AD	10 cycle	No effect	No effect	No effect
		OC	10 cycle	No effect	No effect	No effect
Solvent resistance	Acetone	AD	30 min.	Slight wrinkle	Slight wrinkle	Bubble formation
		OC	30 min.	No effect	No effect	No effect
	Toluene	AD	30 min.	Wrinkle	Wrinkle	Bubble formation
		OC	30 min.	Wrinkle	Wrinkle	Bubble formation
	Methanol	AD	30 min.	Slight wrinkle	No effect	Bubble formation
		OC	30 min.	No effect	No effect	No effect
	Ethyl acetate	AD	30 min.	Slight wrinkle	Slight wrinkle	Bubble formation
		OC	30 min.	Slight wrinkle	Slight wrinkle	No effect

AD: Air-dried (72h, at room temp.) OC: Oven-cured (1h, at 110°C).

As seen in Table 16, all paint films were either unaffected or only slightly affected by solvents. The air-dried reference alkyd paint film was somewhat affected by acetone, toluene, and ethyl acetate showing little wrinkling on the surface, and it was not affected by methanol in any way. At the end of oven-curing, some improvement was observed in the solvent resistance of reference alkyd paint films, and the resistance of the paint film against acetone increased. In the case of waste PET-based alkyd paint, the films were slightly affected by all solvents, and little wrinkling was observed on the film surfaces. At the end of oven-curing, some improvement was observed in the solvent resistance of waste PET-based alkyd paint films, and the methanol and acetone resistance of PET-based alkyd paint films became excellent. Commercial alkyd paint films were also affected by all solvents, and the level of this effect was higher than that observed in both the waste PET-based and reference alkyd paint films. Similarly, the solvent resistance of these commercial alkyd paint films also improved slightly with oven-curing.

The changes depending on ambient effects on the paint film surfaces were observed at the end of the environmental resistance test, which was performed in 10 cycles in 3 stages: 18h in distilled water at room temperature, 3h in the deep freezer at -20°C, and 3h in the oven at 50°C (as summarized in Table 10). As seen in Table 16, at the end of this test, which simulates the change in environmental and atmospheric (or climatic) conditions in an accelerated manner, all air-dried and oven-cured waste PET-based, reference, and commercial alkyd paint films have demonstrated excellent resistance.

When solvent resistance and environmental resistance properties are evaluated together, it has been observed that the paint films having excellent environmental resistance, and relatively high solvent resistance are obtained from waste PET-based, reference, and commercial alkyd paints. The use of waste PET-based alkyd resin in paint formulation did not cause any negative effects of chemical resistance property. It is also possible to say that waste PET-based alkyd paint films are less affected by solvents than commercial alkyd paint films.

Corrosion resistance of oven-cured paint films

Corrosion resistance (salt spray test) of oven-cured paint films (at 110°C for 1h) was determined using a salt-fog corrosion test chamber for 6h. Test results of the salt spray test are presented in Table 17.

Table 17. The results of corrosion resistance test.

Test	Drying method	Time	PET-paint	REF-paint	COM-paint
Corrosion resistance (salt spray test)	Oven-cured	6h	No effect/no rust	Wrinkle/no rust	No effect/no rust

The changes on the cross-hatched (X) paint film surfaces and metal substrates were observed at the end of the salt spray test, which was applied in the salt-fog corrosion test chamber at 35±2°C using NaCl solution (5% wt.) duration of 6 h (as summarized in Table 10). As seen in Table 17, no effect on the anticorrosive added PET-based film and no corrosion/rust of the substrate was observed, and the corrosion test outcomes of waste PET-based paint were found to be comparable to those of commercial alkyd paint. Oven-cured waste PET-based alkyd paint film has demonstrated excellent resistance to corrosive conditions, while wrinkle formation is observed in the reference paint film.

Conclusion

The purpose of this comparative study is to investigate the use of waste PET bottles in the production of solvent-based synthetic paints. For this purpose, the study was conducted in four stages.

In the first stage, the glycolysis reaction of ground waste PET, obtained from post-consumer water bottles, was carried out at atmospheric pressure and high temperatures. The acid and hydroxyl values of the purified intermediates (fractions) obtained by extraction of raw depolymerization product with hot water, were determined by the volumetric method. In the second stage, the waste PET intermediate obtained by glycolysis reaction of waste PET (BHET), was used as a diol component for the production of a four-component PET-based alkyd resin with an oil content of 60%. In the third stage, “waste PET-based alkyd resin”, “reference alkyd resin” which did not contain waste PET, and "commercial alkyd resin" were used as a binder in paint formulations. In the fourth and last stage, at first, the wet paint properties of the paints were determined. Subsequently, the physical coating properties (dry paint film properties) were investigated. In addition, chemical coating properties (household chemicals resistance) and chemical performance tests (solvent resistance, environmental resistance, corrosion resistance) of paint films were also examined.

The following conclusions can be drawn from the obtained results:

- The hydroxyl values of depolymerization intermediates were found to be 445 and 250 mg KOH g^{-1}, respectively. When these results were evaluated together with the results of DSC analyses, it was seen that hydroxyl-terminated monomer, bis (2-hydroxyethyl terephthalate) (BHET) and its dimer were formed in the glycolysis reactions of waste PET.
- The obtained BHET was used completely instead of EG as the diol component in the waste PET-based alkyd resin synthesis reaction successfully. A homogeneous and clear waste PET-based alkyd resin was obtained.
- The use of waste PET-based alkyd resin as a binder in the solvent-based paint system was achieved without any problems. A stable waste PET-based alkyd paint system in which the paint components are miscible and compatible with each other was obtained.
- The viscosity, density, hiding power, and particle size values of the paint prepared with waste PET-based alkyd are in the appropriate range for paint applications. Incorporating waste PET intermediate did not adversely affect the wet paint properties. In fact, the hiding power of waste PET-based alkyd paint is superior to that of both the reference and commercial alkyd paints.
- Waste PET-based alkyd paint film reached the 6^{th} drying degree (hard-dry stage) after 48h at room temperature. Glossy, relatively soft, flexible paint films, having excellent adhesion strength and impact resistance with relatively high abrasion resistance, were obtained from waste PET-based alkyd paints. Hardness values were slightly improved by oven-curing. The use of waste PET-based alkyd resin in the paint formulation did not cause any negative effects on the physical surface coating properties.
- The household chemicals resistance of waste PET-based alkyd paint is better than that of the paint prepared with commercial alkyd. While the paint prepared with commercial alkyd is slightly affected by all test solutions, the cold water, acid, and detergent resistance of waste PET-based alkyd paint is excellent. Waste PET-based alkyd paint was resistant to alkali and basic soap solutions for 48 h. Hot water, alkali, and soap solution resistances were slightly improved by oven-curing. Additionally, waste PET-based alkyd paint has excellent ethyl alcohol, vinegar, and beverage resistance.
- Waste PET-based alkyd paint was slightly affected by all tested solvents, and minimal wrinkling was observed on the film surfaces. However, a slight improvement in solvent resistance was observed at the end of oven-curing. Thus, its resistance to methanol and acetone became excellent. Overall, the waste PET-based alkyd paint was less affected by solvents than commercial alkyd paint.
- The environmental resistance of waste PET-based alkyd paint is excellent, and the oven-cured waste PET-based paint showed excellent resistance to corrosive conditions.
- Including waste PET-based alkyd resin the paint formulation did not generate any unfavorable results on chemical surface coating properties and chemical performance tests. The results of PET-based alkyd paint were comparable to those of commercial alkyd paint. Moreover, it was even better in some cases.

As a result, the use of waste PET-based polymeric binders, derived from the depolymerization intermediates of PET bottles, presents a promising alternative to traditional paint binders in the paint industry. This evaluation of PET waste allows for the sourcing of cost-effective raw materials for the preparation of the paint binders. Consequently, this approach is significant in terms of economic benefits, environmental impact, efficiency, and sustainability.

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