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Research article

Modification of waste PET based alkyd resins with aldehyde and ketone resins: A comprehensive and comparative study

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Abstract. This study aims to develop alkyd-aldehyde and alkyd-ketone blends by modification of waste poly(ethylene terephthalate) (PET) based alkyd resin with urea-aldehyde (UA) and cyclohexanone formaldehyde (CHF) resins for use in coating applications. PET flakes were depolymerized by simultaneous hydrolysis-glycolysis reaction, and depolymerization product (DP) was used completely instead of the diol in the alkyd synthesis. For comparison, reference alkyds without PET were also synthesized. The effect of modifier resin at different ratios and the presence of DP on the coating and thermal properties of blend films were investigated. Medium-hard/hard and gloss/high gloss films with excellent adhesion and impact resistance were obtained from both blends. These films also demonstrated superior chemical and environmental resistance. Blends with CHF resin had better alkali resistance than those with UA resin. In PET-based blends, thermal resistance significantly increased with the addition of the CHF resin to the alkyd resin. Notably, the use of DP did not show a negative effect on the properties of alkyd resin and blend films. On the contrary, much better results were obtained than the alkyd resin alone. Overall, the modification with UA and CHF modifiers and using DP improved the coating properties of the blends. These blends are expected to be considered a sustainable and environmentally friendly alternative for designing versatile coatings for various applications.

Keywords: *poly(ethylene terephthalate), recycling, alkyd, aldehyde, ketone, coating properties, thermal properties*

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1. Introduction

1.1. Poly(ethylene terephthalate) and recycling

Poly(ethylene terephthalate) (PET), a thermoplastic and semi-crystalline polyester, is widely used in the packaging industry (bottling of carbonated drinks and packaging of fruit juices) as well as in fiber and film technology due to its properties such as high chemical resistance, high strength, low gas permeability, low water absorption, and high light transmittance [1, 2]. In recent years, PET waste has become a major problem for the global ecological system due to the widespread use of PET-based materials. Intensive studies focused on waste management have been prioritized to address this issue [3–9]. PET is a recyclable plastic and research into chemical recycling to produce functional products has gained significant attention as a potential solution to the waste PET problem. Both the recycling of waste and the use of recycled products in the production of an economically beneficial product are important for sustainability, the economy, and environmental protection. PET recycling is carried out using four different methods known as primary, secondary, tertiary, and quaternary recycling. It can also be classified as mechanical recycling (primary and secondary recycling), chemical recycling (tertiary recycling) and energetic recycling (quaternary recycling). Primary recycling involves the use of pre-consumer industrial scrap. Instead of discarding the industrial scraps generated during PET production, they are processed with the original PET to obtain products of the same

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quality. This method is a simple, low-cost, and popular approach. Secondary recycling involves the use of post-consumer waste and can also be referred to as mechanical or physical recycling. It includes processes such as grinding, melting, and reforming. However, the properties of PET deteriorate in each cycle, leading to the production of secondary-quality products. In tertiary recycling (chemical recycling), PET waste is chemically processed, and the resulting components are reprocessed for reuse in production. PET can be broken down into monomers and oligomers using various agents such as water, alcohol, glycol, and amine. Quaternary recycling involves burning plastic waste in incinerators in a controlled manner in the air atmosphere, thereby utilizing thermal energy. The chemical recycling of PET can be carried out through reactions such as hydrolysis, glycolysis, methanolysis, aminolysis, and ammonolysis or by performing these reactions simultaneously [3–9]. Thus, functional products are obtained to be used as raw chemicals for the production of different areas. Studies on the use of chemical recycling products of waste PET as raw materials in valuable products such as coating, paint, or alternative adsorbents are reported in the literature [10–28]. In these studies, depolymerization products obtained by chemical recycling of waste PET have been used for syntheses for various resins such as solvent-based and water-based alkyd resins [12, 13, 17–25], unsaturated polyester resin [26, 27], polyurethane resin [11, 28], and epoxy resin [14]. As seen in the literature, the use of waste PET recycling products as raw materials in alkyd resin synthesis is one of the important fields of study, and new studies on this subject are still ongoing. The current focus of these studies is on integrating waste PET products into the alkyd structure while maintaining or even improving the resin's superior properties. It is possible to utilize intermediates obtained from various chemical recycling reactions of post-consumer PET bottle flakes to produce synthetic, and water-reducible alkyd resins with short, medium, and long oil. Studies have shown that using waste PET intermediates instead of one or more components in the alkyd formulation can result in PET-based alkyd resins exhibiting physical, chemical, and thermal properties comparable to those of standard alkyd resins. In some cases, the properties of the PET-based alkyd resins even surpassed those of the standard alkyds. Moreover, using intermediates or raw depolymerization products of waste PET in alkyd resin synthesis provides significant environmental benefits and economic gains. This substitution helps reduce waste and turns the waste of PET bottles, which are pollutants that create a large volume of pollution, into economic value through recycling. The diol component in the alkyd formulation can range from 15 to 30% of the total alkyd reaction charge, depending on the formulation and oil percentage used. Substituting the 150–300 kg diol used in each 1 t batch with waste PET intermediate during large-scale production will significantly contribute to the recovery and utilization of waste PET bottles and the economy of the process.

1.2. Alkyd resins and modifications

Alkyd resin is a thermoplastic polyester resin modified with oil or fatty acids. It is formed through the polycondensation of components, including polybasic carboxylic acids or their anhydrides, polyhydric alcohols, and fatty acids or triglyceride oils [29, 30]. According to the oil length (percentage of oil amount), alkyd resins are classified into three groups: long-oil (>60%), medium-oil (40–60%), and short-oil (<40%) (according to DIN 55 945). Long-oil alkyd resins have numerous unsaturated bonds in their structures due to their high content of fatty acids. However, they dry relatively slowly. They are commonly used in the production of decorative and house paints, as well as in anticorrosive paints and printing inks [31, 32]. Medium-oil alkyd resins are synthesized using drying oils and fatty acids and are generally employed in air-drying paints, industrial paints, and automotive repair paints [29]. Short-oil alkyd resins are prepared using non-drying oils such as coconut oil, peanut oil, or fatty acids. Due to their low fatty acid content, they are challenging to cure through oxidation. Typically, their curing is achieved by preparing blends with resins containing reactive groups that can react with the hydroxyl groups in the alkyd resin structure. These resins are used in the production of oven-cured paint (*e.g.*, metal, radiator, bicycle, and automobile top coat paints) with amino resins [29, 32]. The properties of alkyd resins vary depending on the combination of polyester and oil in their structure. While the polyester group in the alkyd structure is responsible for physical (surface) drying and resistance to weather effects, the oil component is responsible for properties such as film flexibility and oxidative drying (cross-linking). Generally alkyd resins have superior properties such as self-curing at room conditions, compatibility with other resins having a wide spectrum of dissolution in solvents, good pigment-wetting properties, and good flow properties. However, alkyd resins have weak properties such as poor alkali resistance, high yellowing tendency, rapid loss of gloss, and low drying properties [31–33]. Nowadays, it is possible to develop the properties of alkyd resin for its specific uses and even enhance some of its properties. The most effective way to improve the weak properties of alkyd resin and further develop its existing properties is by modifying the alkyd structure using different chemicals. This modification can be physical or chemical [29–35]. The physical modification process is the preparation of blends of some resins with alkyd resin in various ratios. The chemical modification process is the addition of the modifying agent to the reaction medium during the synthesis of alkyd resin [29–35]. There are several studies in the literature on the modifications of alkyds with acrylic [36], urethane [37], epoxy [38], amino [39–41] phenol [42], styrene [43], and silicone [44]. However, there are very few studies on the modifications of alkyds with aldehyde [45, 46] and ketone [47–51] resins.

1.3. Urea-aldehyde resins and related literature

Urea-aldehyde resin, which is in the low molecular weight varnish resin class, is an amorphous resin synthesized by the condensation reaction of urea, isobutyl aldehyde, and formaldehyde. It has a high solubility in solvents such as alcohols, esters, ketones, and aromatic hydrocarbons. It forms compatible systems with most resins, including alkyd resin. Its usage area is wide due to its high solubility and compatibility. Urea-aldehyde resin improves properties such as gloss, hardness, adhesion, resistance to yellowing, heat resistance, water resistance, and pigment wetting, depending on the system it is applied to. Since it is very heat-stable, it can be used in baking finishes without odor and discoloration. It is also used in industrial, metal, automotive paints, and wood coating systems [45–54]. The literature contains few studies on the synthesis and structural analysis of urea-aldehyde resin [52, 53] or its different uses [55–57], but there are only two studies [45, 46] on urea-aldehyde and alkyd combinations for coatings applications. However, no recent study on this subject has been found. The existing studies in the literature on this subject are as follows. Gutkin's patent study is related to modified urea-aldehyde products prepared with various aldehydes such as acetaldehyde, formaldehyde, butyraldehyde, propionaldehyde, and crotonaldehyde. In this patent, for alkyd modification of urea-aldehyde resin, any aldehyde suitable for alkyd resin production, any unmodified polyhydric alcohol, and any polybasic carboxylic acid have been used. The main goal of the invention is to connect the alkyd reactions to a urea-aldehyde condensate, and this process has been carried out *in situ* during synthesis. The urea-aldehyde condensation product resin was first reacted with polyhydric alcohol and then with polybasic carboxylic acids. An esterification reaction of this reaction product with monocarboxylic acids was then performed. As a result of the study, a viscous and clear urea-aldehyde alkyd product resin was obtained, which has been used as an adhesive and plasticizer for nitrocellulose resins [45]. In a patent study conducted by Fischer *et al*. [46], paint formulations containing urea-aldehyde resin were prepared for use as a binder. In the mentioned patent, urea-aldehyde polycondensate was added to the paint formulations along with two different long-oil alkyd resins, not exceeding 20% of the total formulation. The application of these formulations to wood and metal surfaces resulted in the production of high gloss and yellowing-resistant films.

As can be seen from the summary given above, none of the existing studies involve the preparation of coating material by blending the urea-aldehyde resin and alkyd resin, which was presented in our study. In addition, there is no use of waste depolymerization products in the existing studies. In these respects, the aldehyde-alkyd blends prepared in our study are completely different from the literature and are new.

1.4. Ketone resins and related literature

Ketone resins are the product of the condensation reaction of cyclic ketones. They have a wide solubility range and high compatibility with other resins. Their molecular weight is low and in the range of 1000 g/mol. These resins are used as additives to modify the properties of high molecular weight film formers in the coating industry. Cyclohexanone formaldehyde (CHF) resin among ketone resins is used in many areas due to its high polarity and good pigment-wetting properties. It is soluble in alcohol, ester, ketone, ether acetate, and some aromatic hydrocarbons. CHF resin, which is compatible with many resins, has good pigment-wetting properties and comprehensive solubility and it improves properties such as gloss, drying properties, hardness, adhesion, UV resistance, and weather resistance depending on the system to which it is applied. CHF resin is compatible with most resins, including alkyd resin. When used as printing ink with alkyd resin, it increases adhesion, gloss and drying time [56, 58–60]. There are very few studies in the literature about CHF resin-alkyd resin combinations [47–51]. However, no recent study on this subject has been found. The existing studies in the literature on this subject are as follows. The Ortelt *et al*. [47] patent study discusses the development of a ketone-aldehyde resin with broad compatibility. This resin is made up of cycloaliphatic ketones and is intended for use in compositions such as paints, printing inks, and coatings, especially in pigment preparations that require a hard resin. The study describes the synthesis of four different resins through the reaction of alkyl-substituted cyclohexanone with aliphatic aldehydes and ketones in the presence of an alkali catalyst. These resins were then tested for solubility, compatibility, and pigment-wetting properties. The results showed complete solubility in various solvents such as ethanol, n-butanol, butyl glycol, methyl ethyl ketone, ethyl acetate, butyl acetate, xylene, white spirit, n-hexane, and mineral oils. Compatibility tests revealed that the resins were compatible with acrylate, epoxy, melamine, nitrocellulose, polyester, short and long-oil alkyd resins in a 40/60 weight ratio of ketone-formaldehyde resin to resin. The pigment wetting test involved using one of these resins to prepare pigment pastes in various colors, and these pastes were then incorporated into alkyd resin paint without any issues. The resulting coating materials exhibited good rheological properties and flocculation stability, with paint films in different colors achieving gloss values of 83–88% at a 20° angle and 89–92% at a 60° angle. Azimi *et al*. [48] conducted a study in which two different alkyd formulations were synthesized using a mixture of palm oil and castor oil, and a mixture of palm oil and linseed oil. Alkyd-CHF combinations were then prepared with the alkyd resin as the dominant phase, at ratios of up to 50/50 (w/w). The study investigated changes in coating properties such as drying time, hardness, gloss, and chemical resistance based on the ketone resin ratio. The study found that the best properties were observed in the alkyd/ketone combination at a ratio of 70/30% (w/w). Patel *et al*. [49] accomplished a study in which combinations of alkyd resin, ketone (CHF) resin, and castor oil-epoxy resin condensate, were prepared in different CHF resin weight ratios (10, 20, 30%) while keeping the amount of alkyd resin constant. The films of these combinations dried at room temperature and exhibited good mechanical and chemical resistance. In a study conducted by Athawale *et al*. [50], it was observed that significant improvements in adhesion, hardness, gloss, storage stability, acid resistance, and drying time were obtained when the optimum ratio of ketone (CHF) resin (30% w/w) was blended with linseed oil-based long-oil pentaerythritol-phthalic anhydride alkyd resin. In a similar study also performed by Athawale *et al*. [51], refined linseed oil-based long-oil aliphatic glycerin-adipic acid alkyd and ketone (CHF) resin blends were prepared at different ratios. The study indicated that the drying, hardness, gloss, and adhesion of the blend at a 50/50 ratio were better, and the storage stability of blends containing 20% ketone resin was increased. No change was observed in blends containing less than 10% ketone resin. Apart from these, we have a recent study on alkyd-melamine-ketone systems. In our previous study, alkyd-amino resin (Alkyd-MF), prepared using short-oil coconut oil fatty acid (COFA) alkyd resin based on waste PET with melamine formaldehyde resin, was blended with the CHF resin at different ratios. At the end of the study, Alkyd-MF/CHF blend coatings with good physical and excellent chemical coating properties were obtained. Coating and thermal properties were improved by adding the CHF resin to the alkyd-MF, and with the addition of CHF resin, individual alkali resistance of alkyd and physical coating properties of blends increased [61].

As can be seen from the summaries of studies about CHF resin and alkyd resin combinations given above, it was observed that there is no study on the physical modification of alkyd resin synthesized using waste PET with CHF resin, except for our previous work. In this study, for the first time, four-component, long-oil TOFA-based, and waste PET-containing alkyd resin/ketone (and alkyd/aldehyde) resin blends were prepared. Then, the coating and thermal properties of these blends were examined in detail and compared to their counterparts without waste PET. In this respect, this study is completely different from the existing studies and is new.

1.5. The purpose of this study and methodology

Green technology evaluates sustainable environmental applications, solid waste management, and recycling processes together. The main principles of green technology and green economy are reducing, reusing, and recycling manufacturing products [61–66]. By this approach, this study focuses on waste management, green technology, sustainability, and efficiency. In this context, the goal of this study is to design alkyd-aldehyde and alkyd-ketone blends for versatile coatings that may be used in various applications using post-consumer PET bottles with a green technology approach. To the best of our knowledge, no detailed and comprehensive experimental study has yet been reported in the literature on preparing alkyd-aldehyde and alkyd-ketone blends using four-component, long-oil TOFA-based alkyd resin containing waste PET depolymerization product. Within the scope of this study, unpurified waste PET depolymerization product (oligomer mixture) was used completely instead of the diol component of alkyd resin. Then, blends of the synthesized waste PET-based long-oil alkyd resin both aldehyde resin and ketone resin were prepared in various ratios. For this, firstly, all resins were diluted in the presence of suitable solvents. Secondly, the alkyd resin was blended with aldehyde (UA) resin for alkyd-aldehyde blends and with ketone (CHF) resin for alkyd-ketone blends. Afterwards, the coating and thermal properties of both waste PET-based alkyd-aldehyde (ALK-UA) and alkyd-ketone (ALK-CHF) blends were investigated by comparing them with reference counterpart blends prepared in the same way without PET intermediate. This study differs from similar studies because it is focused on the comparative study of both alkyd-aldehyde and alkyd-ketone systems prepared using alkyd resin (with or without PET), UA resin, and CHF resin for the first time. Compared to existing literature, in this study, both alkyd-aldehyde and alkyd-ketone combinations offer durable coatings with improved properties such as 100% adhesion, good mechanical properties, high gloss, excellent chemical resistance, and thermal stability. Moreover, the use of recycled PET in both alkyd-aldehyde and alkyd-ketone systems is an innovative advantage of this work. This approach supports environmentally friendly green applications by recycling PET waste, provides sustainability, efficiency, and economy, and can also contribute to developing durable coatings for various applications. The methodology scheme of this study is presented in Figure 1.

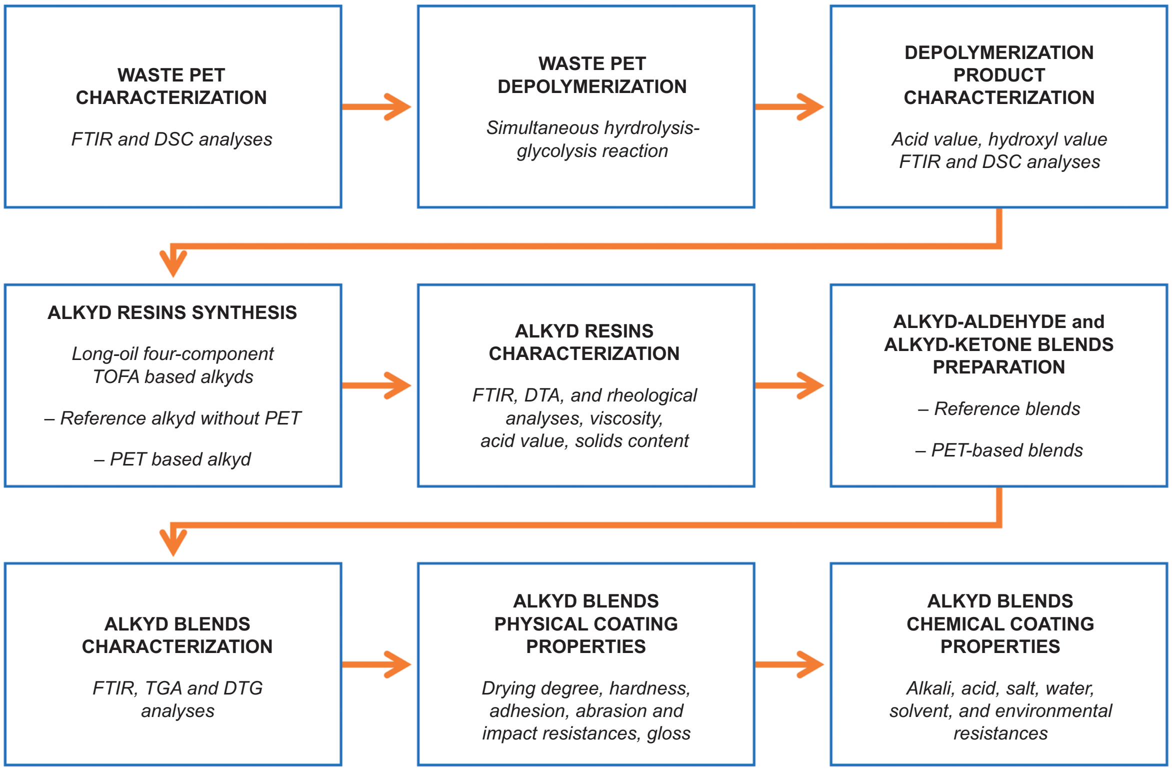

Figure 1. The methodology scheme of this study.

2. Experimental

2.1. Materials

Waste PET flakes obtained from grinding of post-consumer bottles (8 to 10 mesh fraction) were used in the study. Post-consumer PET water bottles were collected and preserved by ourselves. They were not contaminated with other waste. Then, the caps and labels of these bottles were removed, washed with distilled water, dried and ground. The viscosity average molecular weight (M_v) of PET flakes was previously calculated to be 37 000 in our unit's laboratory using the Mark–Houwink equation [13, 67–69]. The intrinsic viscosity (η) measurements were performed with Ubbelohde Viscometer (Cannon IB E541) in tetrachloroethane/phenol (40/60, v/v) mixture at 25 °C according to Huggins and Schulz–Blaschke method [67–69]. The η value of waste PET bottles is about 0.7–0.8 g/dL. Commercially, PET has an intrinsic viscosity in the range of 0.45 to 1.2 g/dL and a poly dispersity index (PDI) of around 2 [70, 71]. Molecular weight distribution parameters obtained by GPC (gel permeation chromatography) analysis of PET have been investigated previously [72–76]. In related studies, the dispersity (PDI: M_w/M_n) has been reported as 2.08, 2.42, 2.19, 2.59 and 3.38.

Tall oil fatty acid (TOFA) coded Sylfat 2S was provided by Arizona Chemical Ltd. (a Kraton company, USA). Aldehyde (urea-aldehyde) (UA) resin coded Laropal A81 was supplied from BASF Coatings GmbH (Germany). Ketone (cyclohexanone formaldehyde) resin (CHF) coded Polytone K-96 was supplied from Worlée-Chemie GmbH (Germany). The physical properties of commercial COFA, UA and CHF resin in the technical data sheets are presented in Table 1.

Phthalic anhydride (PA) and glycerine (GLY) were products of Sigma-Aldrich Chemie GmbH (USA), and dipropylene glycol (DPG) was the product of Merck KGaA (Germany). The purity assays of crystal form phthalic anhydride, viscous liquid glycerine and liquid dipropylene glycol are 'for synthesis', '83.5–89.5%', and 'for synthesis (mixture of isomers)', respectively. Dryers (6% zirconium octoate (AKDRY Zr Octoate), 6% manganese octoate (AKDRY Mn Octoate), 24% lead octoate (AKDRY Pb Octoate)) were products of AKPA Chemicals (Turkey). The rest of the materials were synthesized or analytical grade, and distilled water was used throughout the study.

2.2. Instruments and equipment

The laboratory-type high-pressure reactor system

Depolymerization of waste PET by simultaneous hydrolysis-glycolysis reaction was carried out in the Stainless Steel Autoclave (Berghof brand, BR-1000 model, Berghof Products+Instruments GmbH, Germany) at high temperature and high pressure. The laboratory-type high-pressure reactor system (autoclave) has a cylindrical chamber made of steel (316Ti) with a volume of approx. 1750 mL and a stirrer that can reach a stirring speed of 0–500 rpm. The reactor head contains a stirrer motor, thermocouple, pressure gauge, safety hose, and sampling valves. The system has a safety belt and Teflon seal with a control panel where temperature, pressure, stirrer speed, and reaction time can be adjusted. Heating is done with a jacket containing an electric heating plate. The autoclave can operate at a wide range of pressures up to 200 bar and temperatures up to 300 °C.

Differential scanning calorimetry (DSC)

DSC analysis of waste PET flakes and depolymerization product (DP) was performed by DSC (Hitachi brand, Nexta DSC200 model, Hitachi High-Technologies Corporation, Japan). The measurements were carried out by heating ~10 mg of sample from –80 to 300 or 400 °C at a heating rate of 10 or 20 °C/min in the nitrogen atmosphere.

Fourier transform infrared spectroscopy (FTIR)

The structural analyses of the waste PET flakes, depolymerization product (DP), alkyds and blends

Table 1. Physical properties of COFA, UA resin and CHF resin.

Physical properties of TOFA	Value	Physical properties of UA resin	Value	Physical properties of CHF resin	Value
Acid value	193–196 mg KOH/g	Acid value	≤3 mg KOH/g	Acid value	≤0.5 mg KOH/g
Saponification number	197 mg KOH/g	Hydroxyl value	~40 mg KOH/g	Hydroxyl value	230–250 mg KOH/g
Iodine number	152 cg I/g	Saponification value	~65 mg KOH/g	Iodine number (50% solution in alcohol)	≤1.0
Density at 20 °C	0.950 g/cm^3	Iodine number	≤3	Flow time (50% solution in alcohol) B4 Ford-Cup	20–23 s
Viscosity at 2 °C	25 cP	Density at 20 °C	1.11 g/cm^3		

were performed by FTIR (Agilent brand, Cary 630 model, Agilent Technologies, Inc., USA. The IR spectra of samples were obtained in the range 500–4500 cm^{-1}. To prepare the measurement pellets, we diluted the samples with IR grade KBr (sample/KBr: 1/200 (w/w)). Some of the measurements were performed by FTIR (Jasco brand, FT/IR 4700 model, Jasco International Co., Ltd., Japan) with ATR unit.

Rheometer

The rheological measurements of the alkyds were performed by rheometer (Anton Paar brand, MCR 102 model, PP25 measuring system, Anton Paar GmbH, Austria). The set values were as follows: ramp shear rate 1–100 s^{-1} at 25°C.

Thermogravimetric analyzer (TGA)

The thermal behaviors of the blends (for TGA/DTG analysis) and alkyds (for DTA analysis) were performed by TGA (Linseis brand, STA PT 1750 model, Linseis Messgeraete GmbH, Germany). The measurements were made by heating ~10 mg of the sample from ambient temperature (20–25 °C) to 800 °C at a rate of 10 °C/min in an air atmosphere.

Surface coating test equipment

The physical coating properties of the blends were performed with standard-compliant coating test equipment with relevant standards. The general properties of the equipment are briefly described below.

Drying tester

The drying degrees of the blend films were determined using the ‘Drying Tester’ (Erichsen brand, 415/E model, Erichsen GmbH & Co. KG, Germany). The equipment consists of glass beads with a diameter of 0.2 mm, load weights (20 and 200 g) with a diameter of 24 mm, and a force application cylinder attached to the stand. The compression spring of the cylinder generates a stamping force maximum of 250 N. The force is applied to the coating by a lever mechanism, perpendicularly.

Pendulum hardness tester

The hardness values of the blend films were determined using the ‘König Pendulum’ (Sheen brand, 707K model, Sheen Instruments Ltd., England). König pendulum, which is housed in a plexiglass case to prevent air movement, consists of a triangular-shaped pendulum with a counterbalance that adjusts the period of oscillation to 1.4 s. Two 5 mm diameter ball bearings are in contact with the test surface while oscillating. The equipment’s scale is marked at the relevant angles (6° and 3°) to the test specifications, as well as zero points. A photosensor positioned at these limits records the pendulum’s oscillations. The signals from the photosensor are recorded by an automatic electronic counter, and the result is displayed digitally.

Cross-cutter for adhesion test

The adhesion values of blend films were performed by the ‘Cross-cutter’ (Erichsen brand, GS 10 model, Erichsen GmbH & Co. KG, Germany). This manual instrument is a simple hand-held unit. It consists of a cutting head containing six cutting blades (6 edges, cutting distance 1 mm) and a wooden hand grip. Magnifying glass and bristle brush are included in the test kit. It works purely mechanically and is used to perform adhesion inspections.

Falling sand abrasion tester

The abrasion values of blend films were performed by the ‘Falling Sand Abrasion Tester’ (Erichsen brand, 2511-11 model, Erichsen GmbH & Co. KG, Germany). This model device consists of three main parts. These are a sand reservoir (20 cm diameter) that includes a 60° taper funnel, a guide tube (height × inner diameter: 91.5×29 mm), and a bottom receptacle that includes specimen place (where the coated plate will be positioned), and container for sand to be collected. The guide tube extends between the funnel and the plate. The distance between the end of the guide tube and the plate’s surface is 3.5 cm. The coated plate is fixed under the guide tube at a 45° angle. A sturdy base and support system hold the apparatus in a vertical position.

Impact (flexibility) tester

The impact values were determined by the ‘Impact (flexibility) tester’ (BYK Instruments brand, PF-1115 light-duty model, BYK-Gardner GmbH, Germany). The instrument basically consists of a guide tube and a sturdy aluminum-cast base stand. The graded guide tube (100 cm) is hanging vertically in the upper arm of the solid base stand. The base stand has support with a 1.5 cm diameter hole on which the plate is placed. There is a slot inside the guide tube for the standard steel rod weights (1 and 2 kg) to slide. To facilitate readings, the slot has been scaled along the guide tube. The panel to be tested is placed between the punch and the anvil over the base stand.

Gloss meter

The gloss values were determined by the 'gloss meter' (Sheen brand, 101N model, Sheen Instruments Ltd., England). In this model device, gloss at a specific angle is measured by comparing the specular reflectance of the coating with that of black glass. A gloss meter is a device that measures the gloss level of the surface and provides numerical data to support the visual perception of surfaces and coatings. For this, the light should be transmitted onto the surface at an appropriate angle to the average gloss level of the surface. The single-angle gloss tester, which is designed with the light source and detector positioned at a 60° angle to the surface being measured, is suitable for most applications.

2.3. Methods

2.3.1. Depolymerization reaction of PET

As given in the literature, the depolymerization of PET can be carried out various reactions such as hydrolysis, glycolysis, methanolysis, aminolysis, and ammonolysis [3–7]. Glycolysis is a widely used commercial process for PET. As a result of the reaction of PET with ethylene glycol at 180–250 °C, it is possible to obtain PET monomers (bis(2-hydroxyethyl) terephthalate and ethylene glycol) and low molecular weight oligomers. Propylene glycol and dipropylene glycol are also used in glycolysis reactions. PET can also be hydrolyzed and separated into its monomers (terephthalic acid, ethylene glycol). PET, which is quite resistant to hydrolysis under normal conditions, is rapidly hydrolyzed by water at temperatures above 280 °C and under pressure. Hydrolysis of PET can be carried out under neutral conditions with only hot water or water vapor. In addition, hydrolysis is also carried out under alkali and acidic conditions. Alkali hydrolysis is carried out using 4–20% solutions of NaOH or KOH. Acidic hydrolysis is more commonly realized in the presence of sulfuric acid but is also used with mineral acids such as phosphoric and nitric acid. Hydrolytic depolymerization of PET is quite slow compared to glycolysis. Therefore, the biggest disadvantage of hydrolysis is that long periods are required for complete depolymerization. Alcoholysis is a recycling process carried out by reacting waste PET with various alcohols. In case of methanol is used as alcohol, this process is called methanolysis. Dimethyl terephthalate and ethylene glycol, which are not of high quality, are obtained by treating PET with methanol at 185°C in the presence of a catalyst (mostly zinc acetate). Aminolysis is a recycling process carried out by depolymerizing PET waste using different amines. The reaction is usually carried out in aqueous solutions of primary amines. The most preferred primary amines are methylamine, ethylamine, and ethanolamine. In the ammonolysis, terephthalamides are obtained from the reaction of PET with aqueous ammonia in an ethylene glycol medium [3–7, 77–79].

All these reactions used for chemical recycling can also be carried out simultaneously. In the depolymerization of waste PET which used both the glycol and water as reactants together (simultaneous hydrolysis-glycolysis), both the glycolysis reaction and the neutral hydrolysis reaction occur simultaneously as the main reactions. At the same time, some side reactions take place and produce unexpected oligomers and side products. Etherification and advanced etherification reactions which occur during depolymerization, result in water formation, glycol formation, polymers with glycol end groups, and polymers with carboxylic end groups. The high amount of water in the reactant provides dominance of hydrolysis in the depolymerization reaction and contributes positively to depolymerization. In addition, the simultaneous application of both depolymerization reactions, as well as the presence of xylene that can partially or completely dissolve the reaction products, provides some distinct advantages [69]. Here, the equilibrium between the polycondensation reaction of the monomers or oligomers, which occurred by depolymerization with both reactants and the reverse reaction is important. Because hydrolysis and glycolysis are reversible reactions, the equilibrium of the polymerization reaction needs to be changed with the reverse reaction of polyesterification. In the literature, previous studies reported that this equilibrium could be achieved by using an inert solvent such as xylene during hydrolysis or glycolysis reactions. The presence of this solvent during the depolymerization of PET has shifted the equilibrium to depolymerization by causing the oligomeric products to dissolve in the xylene phase during the reaction. This has provided greater degrees of polymerization that is higher conversion at lower temperatures and pressures [67–69]. The effect of xylene usage on depolymerization reactions is important in terms of the composition and distribution of intermediate products [80, 81]. Based on all this information, in this study, PET depolymerization was carried out by simultaneous hydrolysis-glycolysis reaction in the presence of xylene to obtain hydroxyl and carboxyl terminated oligomers using dipropylene glycol (DPG) and water. The reaction conditions were determined by evaluating the results obtained in our previous depolymerization studies performed in our unit in this field with the prediction of high conversion, high yield, ease of reaction, and relatively short reaction time [2, 10–19, 21–23, 36–41, 67–69, 80, 81].

In this context, a simultaneous hydrolysis-glycolysis reaction of waste PET (0.5 mol) with DPG (0.5 mol) and water (60 mL) in the presence of xylene (220 mL) was carried out with the catalysis of zinc acetate (ZnAc, 1 wt% of PET) in a Berghof BR-1000 stainless steel autoclave at high pressure.

Calculations of the amount of reactants were made based on the repeating unit mass (molar mass) of PET is 192 g/mol [71, 82–85]. Waste PET flakes (100 g), which are equivalent to 0.5 mol repeating unit, were added to 69.88 g DPG (0.5 mol) (molar mass = 134.17 g/mol), such that the molar ratio of PET repeating unit to glycol was 1/1. Depolymerization reaction conditions are summarized in Table 2.

The raw product obtained at the end of the depolymerization reaction was decanted to remove the xylene phase, and no other process was performed for purification. Then, it was dried at room temperature and then in a vacuum oven at 60 °C and ground in the agate mortar. For the characterization of the raw depolymerization product (DP), acid value (AV) (ASTM D-1639), hydroxyl value (HV) (ASTM E-222), and DSC analyses were performed.

2.3.2. Preparation of alkyd resins with and without PET

Four-component long-oil (60% oil content) reference alkyd (AREFT) and PET-based alkyd (APETT) resins were prepared by the fatty acid method. The '*K* alkyd constant' system [86] was used in the formulation calculations. The synthesis reactions were realized in a five-necked glass reactor equipped with a mechanical stirrer, a reflux condenser + Dean-Stark part, a gas bubbler, and a thermometer. KOH was used as a catalyst (0.1 wt% of total charge) and xylene as the solvent (10 wt% of total charge). The reactions were monitored by periodic acid value determinations and continued at 220 °C in a nitrogen atmosphere until the desired AI value (10–15 mg KOH/g) was reached. The components of the AREFT and APETT alkyds and their percentages by weight are presented in Table 3.

Table 2. The depolymerization conditions of waste PET (presence with 60 mL water and 250 mL xylene).

PET [g]	DPG [g]	Temperature [°C]	Pressure [bar]	Time [h]
100	69.88	220–225	25–26	3

AREFT alkyd without waste PET was produced using TOFA, PA, GLY, and DPG. The constant *K*, which is the ratio of the total amount of moles to the acid equivalent (m_o/e_A) was 1.15, and the *R*-value, which is the ratio of base equivalent to acid equivalent (e_B/e_A) was 1.05. APETT alkyd, including waste PET, was produced using TOFA, PA, GLY, and DP. DP was completely used instead of diol. *K* constant (m_o/e_A) was 1.15, and the *R*-value (e_B/e_A) was 1.05. In the formulation calculation of PET-based alkyd, the amount of hydroxyl and carboxyl functional DP used instead of the diol component was determined according to its base equivalent. The acid equivalent (acid group content) of the depolymerization product was deducted from the acid equivalent of the PA.

2.3.3. Preparation of alkyd-aldehyde (ALK-UA) and alkyd-ketone (ALK-CHF) blends

The compositions and symbols of all prepared blends are given in Table 4.

ALK-UA blends were prepared by homogeneously mixing alkyd (AREFT and APETT) resins with urea-aldehyde resin (UA) using a high-speed mechanical stirrer. Before blending, the alkyd resins were diluted to 70% solid content, and the UA resin was diluted to 50% solid content with xylene. The alkyd/UA ratios chosen were 95/5, 90/10, 85/15, and 80/20 by weight. ALK-CHF blends were prepared by homogeneously mixing AREFT and APETT

Table 3. The components and weight percentages of AREFT and APETT alkyds.

Component	AREFT alkyd [wt%]	APETT alkyd [wt%]
TOFA (monobasic acid)	56	57
PA (dibasic acid)	23	16
GLY (polyol)	16	16
DPG (diol)	5	–
Depolymerization product of waste PET (DP) (diol)	–	11

Table 4. The symbols and the compositions of the ALK-UA and ALK-CHF blends.

Alkyd-UA blends	Components ratio [wt%]	Alkyd-CHF blends	Components ratio [wt%]
Reference blends	**AREFT/UA ratio**	**Reference blends**	**AREFT/CHF ratio**
AREFT100-UA0	100/0	AREFT100-CHF0	100/0
AREFT95-UA5	95/5	AREFT80-CHF20	80/20
AREFT90-UA10	90/10	AREFT70-CHF30	70/30
AREFT85-UA15	85/15	AREFT60-CHF40	60/40
AREFT80-UA20	80/20	AREFT50-CHF50	50/50
PET-based blends	**APETT/UA ratio**	**PET-based blends**	**APETT/CHF ratio**
APETT100-UA0	100/0	APETT100-CHF0	100/0
APETT95-UA5	95/5	APETT80-CHF20	80/20
APETT90-UA10	90/10	APETT70-CHF30	70/30
APETT85-UA15	85/15	APETT60-CHF40	60/40
APETT80-UA20	80/20	APETT50-CHF50	50/50

resins with cyclohexanone formaldehyde (CHF) resin also using a high-speed mechanical stirrer. Before blending, the alkyd resins were diluted to 70% solid content, and the CHF resin was diluted to 50% solid content with the toluene/cyclohexanone/1-butanol solvent mixture (60/20/20 by weight). The alkyd/CHF ratios chosen were 80/20, 70/30, 60/40, and 50/50 by weight. All blends were kept for a day, and checked whether or not they formed a phase.

2.3.4. Preparation of blend films

The driers were added to the blends at ratios of 0.2% Zr, 0.39% Pb, and 0.1% Mn by weight, depending on the alkyd resin content. Then, the blend films were prepared on glass and metal plates using a 50 µm BYK applicator. Additionally, the blend films were also prepared on glass tubes by dipping and on tin plates by casting technique.

2.3.5. Physical surface coating tests

To determine physical surface coating properties, drying degree (DIN 53150), pendulum hardness (DIN 53157), adhesions strength (ASTM D3359-76), abrasion resistance (ASTM D 968-05), impact resistance (ASTM D 2794-69) and gloss (ASTM D 523) tests were performed according to standards. The general properties of test equipment used in physical coating tests were explained in the Instruments & Equipment section. The test methods (description of the measurements) are presented below.

Drying degree

The drying degree of coatings was determined using the drying tester according to the 'Modified Bandow-Wolff' method. This test gives both an idea about the drying rate and the drying degree of the coatings. The drying degree (or level or stage) is rated from 1 to 7 in this standard. 1st drying degree is determined by the adherence or non-adherence of the glass beads poured onto the coating surface without any load for 10 s. The drying degrees between 2 to 6 are also determined by the adherence or non-adherence of craft paper to the coating when specific loads (range from 5 to 5000 g/cm^2) for 60 s. The unit of measurement is the 'drying degree'. The results are denoted by a number between 1–7 [87].

Hardness

The hardness of coatings was measured by the König pendulum. The pendulum hardness test, which relates the damping of an oscillation to the hardness of surfaces, is based on the principle that the amplitude of the pendulum's oscillation will decrease more quickly on a softer surface. This type of hardness is determined by measuring the mechanical damping of the pendulum oscillating on the coating within the specified limits of amplitude. In other words, the hardness of a coating is the number of oscillations made by a pendulum within specified limits of amplitude. In the test performed by König pendulum, the time it takes for the amplitude to decrease from 6 to 3° is measured. The unit of measurement is 'König second' [87].

Adhesion strength

The adhesion properties of coatings were evaluated by the cross-cutter. The basic principle of this test is to cut through the coating with a series of cuts at right angles in a defined manner. For this aim, several cuts at right angles to each other are created (square-shaped lattice pattern, 6×6 = 36) on the coating surface on a glass panel with the cross-cutter and compared with schematic representations in the standard. Thus, it is evaluated visually by examining how the coating has broken away from the base material (along the cutting edges and/or complete squares). The result is given as an adhesion%. 100% adhesion corresponds to 'completely smooth blades of the cuts, without any loss of coating material' according to the standard. The unit of measurement is % [87].

Abrasion resistance

The abrasion resistance of coatings was determined using the falling sand abrasion tester. In this test method, abrasion is provided with abrasive particles falling through a guide tube and impinging the test specimen until the substrate becomes visible. For this, abrasive hard sand is poured through the vertical tube onto the coating on a glass panel. Abrasion resistance is expressed in terms of the volume of abrasive required to abrade a unit thickness of the coating. Standardized abrasive particles (the hard silica sand, passing through sieve#25 and remaining on sieve#30) are filled into the funnel. The hard sand placed in the reservoir is released to a guide tube by a flow gate key. The sand falls/pours freely onto the plate through the guide tube due to gravity. The volume of sand that eroded a specified thickness of the coating is determined. The results are reported as the volume of sand (measured in mL) required to create a gap of about 4 mm in diameter on the film surface when poured onto the film surface on the plate. The unit of measurement is mL·sand [87].

Impact resistance

The impact resistance of coatings was measured by the impact tester. This tester was designed to test the resistance of coatings, surface damage, and penetration using relatively small impact forces. It also gives an idea about the flexibility of the coatings as well as their impact resistance. Impact testing is a method in which a cylindrical steel weight of standard dimensions is freely dropped onto a coated metal plate through a guide tube, and the coating undergoes rapid deformation. At the end of the test, if the film is sufficiently flexible, it is either unaffected or is affected in a manner lifting off, peeling, or cracking from the surface. For measurement, the standard steel weight (1 or 2 kg) is raised to the desired height using the lift screw and then dropped freely through a guide tube onto a coating on a metal plate from varying heights (max. 100 cm). Then, the damage in the plate is visually inspected for flaking, cracking, and deformation. If no deformation is observed in the coated plate, this process is performed from different heights with different weights by low-power increments until a deformation occurs on the coating on a metal plate. The deformation caused by the falling weight and height is determined, and the test is ended when deformation is observed. As a result of the test, the impact force corresponding to the weight [kg] and height [cm] that causes deformation is determined. This is an impact strength of the coating. The unit of measurement is kg·cm [87].

Gloss

The gloss properties of coatings were evaluated by the gloss meter at 60° angle. This device works on the principle of measuring the amount of the light, which is sent to a surface at a certain angle and in a certain amount, reflected from this surface. For the measurement, first, the device is calibrated using a black glass plate at the angle to be measured. Then, the coated plate is placed in the measuring point of the device, light is sent to the film surface at the desired angle and the amount of the reflected light is determined. The unit of measurement is 'gloss unit (GU)' [87, 88].

2.3.6. Chemical surface coating tests

To determine the chemical surface coating properties, alkali, acid, and salt resistance (ASTM D1647-89), water resistance (ASTM D1647-89), solvent resistance (ISO 2812-3), and environmental resistance [89] tests were conducted in accordance with relevant literature.

The alkali resistance test was carried out by the immersion method. First, the films were prepared by dipping method on glass tubes. Then, the completely dry films were immersed in the alkali solution (0.1 M NaOH and 3 wt% NaOH). Then, they were removed from the solutions at certain intervals and examined visually. Acid, salt, and water resistance tests were also carried out by the immersion method. For the acid resistance test, films were prepared by the dipping method in glass tubes. The films were prepared with an applicator on glass plates for the salt resistance test, while by casting method on tin plates for the water resistance test. Then, the completely dry films were immersed in the solutions (3 wt% H_2SO_4, 5 wt% NaCl, and distilled water at room temperature). Then, they were removed from the solutions at certain time intervals and examined visually. In the case of the water resistance test, the films were immersed and kept in distilled water for 18 h. Then they were examined visually after wiping dry, and following 20 min, 1, and 2 h. In the solvent resistance test, the gauzes (1×1 cm) were dipped into different solvents (acetone, toluene, methanol, ethyl acetate). After removing the excess solvent, they were placed on the coating surface, covered with a petri dish, and waited 30 min according to standard. They were examined visually. Environmental resistance test was performed as follows, as given in the literature: (I) The film on the glass plate was kept in distilled water at room temperature for 18 h. (II) It was kept in the deep freezer at –20 °C for 3 h. (III) It was kept in the oven at +50 °C for 3 h. At the end of these three stages, one cycle was completed. This procedure was repeated ten times.

3. Results and discussion

The appearances of the waste PET flakes and raw depolymerization product (DP) obtained from the simultaneous hydrolysis-glycolysis reaction of waste PET are presented in Figure 2.

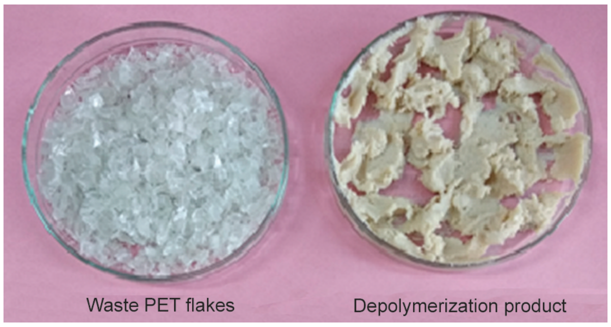

Figure 2. The appearance of the waste PET flakes and DP.

3.1. FTIR and DSC analyses of waste PET

The FTIR and DSC graphs of waste PET flakes are given in Figure 3. In the IR spectrum of waste PET (Figure 3a), the main peak originating from both the OH group and the C=O group is observed at 3430 cm^{-1}. The stretching vibration peaks of the –CH_2– group are observed around 2960 and 2900 cm^{-1}, and the stretching vibration main sharp peak of the C=O group is observed around 1725 cm^{-1}. There are small peaks belonging to the aromatic double bond stretching vibration at 1585 and 1508 cm^{-1}, the –CH_2– bending vibration peak at 1457 cm^{-1}, the in-plane stretching vibration peak of the C–C bond in the phenyl group is observed around 1410 cm^{-1} and the symmetric deformation peak belonging to the –CH_2– groups is observed at 1346 cm^{-1}. At 1269 and 1247 cm^{-1}, there are stretching vibration peaks belonging to the ester bonds in the structure. Additionally, at 1120 and 1098 cm^{-1}, there are double peaks belonging to the C–C stretching in the phenyl group. At 1020 cm^{-1}, there is a peak belonging to the deformation vibration in the aromatic ring, whereas around 973 cm^{-1}, there is a small peak belonging to the carbonyl stretching vibration in the –OCH_2CH_2O– group. At around 871, 800, and 730 cm^{-1} (sharper), there are peaks attributed to the C–H out-of-plane deformation vibration in the aromatic ring [90–92]. All of these are characteristic peaks belonging to PET [37].

In the DSC graph presented in Figure 3b, 1st and 2nd run DSC curves of waste PET flakes are presented

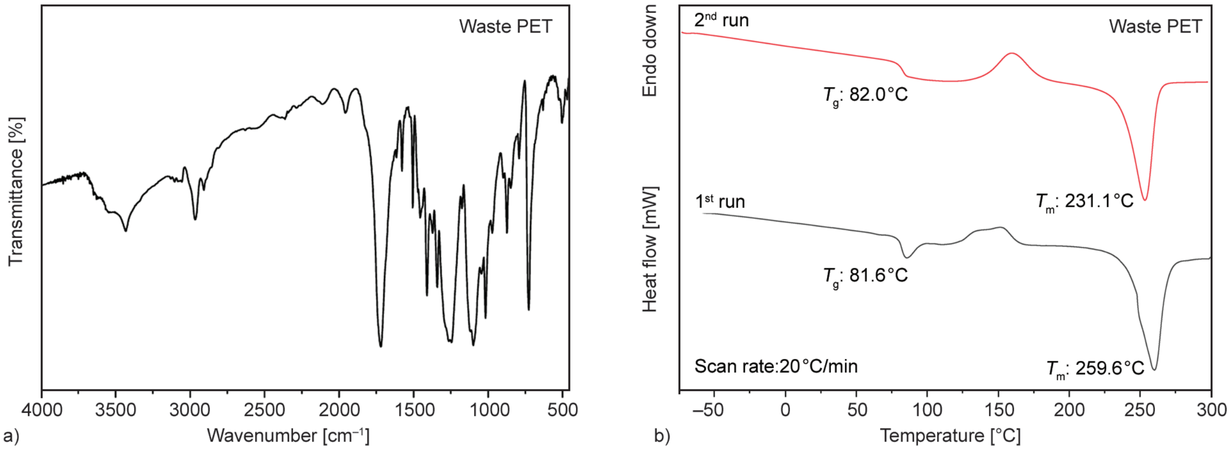

Figure 3. a) FTIR and b) DSC graphs of waste PET flakes.

together. As reported in the literature, in a DSC experiment, the sample is melted and heated beyond the melting point to erase any thermal history completely. Thus, melting of the polymer in the first heating eliminates its history. The first heating (or run) in the DSC analysis shows the history of the polymer, which reflects the preparation, cooling, storage conditions, *etc.,* before the measurement. In contrast, the second heating (or run) provides information about the identity of the sample, after a controlled cooling under defined conditions, and identifies the polymer [93, 94]. In this context, in DSC measurements of waste PET, double runs (1st and 2nd run) were studied. When the DSC curve of waste PET flakes (2nd run) was examined, the glass transition temperature (T_g) was observed at 82 °C and the melting peak (T_m) at 259.9 °C. In addition, there is a crystallization peak at 159 °C. All these peaks observed in the DSC curve of waste PET flakes are consistent with the literature [95–97].

3.2. FTIR and DSC analyses of DP

The FTIR and DSC graphs of DP are given in Figure 4. When the FTIR spectrum of DP, which is the product of a simultaneous hydrolysis-glycolysis reaction carried out in a xylene medium, is examined (Figure 4a), it is seen that the 972 cm^{-1} peak attributed to the ether bond of PET has almost disappeared due to the breaking of the ether bonds of PET. In addition, a new peak is observed around 932 cm^{-1}. This peak attributed to the carboxylic acid OH bending (out-of-plane) probably originates from oligomers with COOH end groups. The peak attributed to the C=O stretching of PET, located at 1720 cm^{-1} has shifted slightly and is observed around 1690 cm^{-1}. In addition, two new peaks belonging to the carboxylic acid OH stretching are located at 2664 and 2531 cm^{-1}. It was also observed that the broad peaks and their intensities attributed to OH groups, observed in the range of 2500–3600 cm^{-1}, changed depending on the oligomeric structures with hydroxyl and carboxyl end groups formed [90–92]. All these changes observed in the spectrum indicate that the waste PET is degraded.

DSC analysis was performed to characterize the oligomers in the composition of the DP. For this, the endotherms observed in the DSC curves were compared with the melting temperatures of PET oligomers given in the literature. Thus, it was determined these endotherms could belong to which oligomers. Here, the temperature shifts that may be observed during the product's melting in the DSC analysis were also considered. As known, the differences between the values observed in the DSC curve of the depolymerization product and the melting points of the oligomers given in the literature are due to the dissolution in each other and co-melting of the monomers, dimers, and oligomers in the product composition during the DSC analysis. In this case, spread endotherms are observed rather than sharp peaks, and shifts occur in melting temperatures [68, 80, 81].

In the DSC graph presented in Figure 4b, there are many endotherms instead of the single sharp melting peak in the DSC curves of DP. These endotherms are the spread endotherm (region 1) extending between 70 and 115 °C with a maximum at 110 °C; the spread endotherm (region 2) extending between 120 and 180 °C with a maximum at 150 °C; the relatively sharp endotherm (region 3) extending between 200 and 280 °C with two maxima at 252 and 272 °C; and

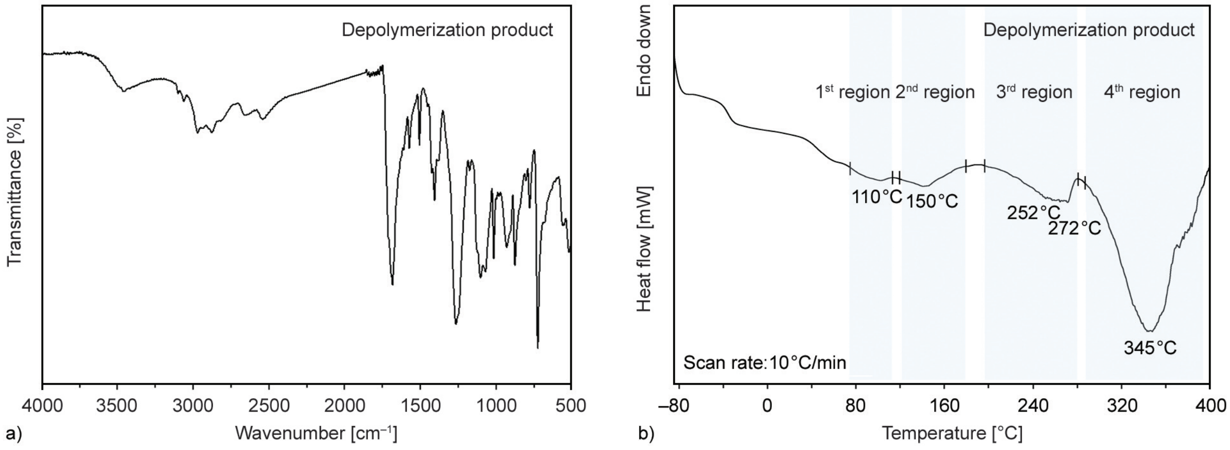

Figure 4. a) FTIR and b) DSC graphs of DP.

the sharp and broad endotherm (region 4) extending between 285 and 400 °C with a maximum at 345 °C. The presence of more than one endotherm can be attributed to many oligomeric structures having different end groups. When these endotherm regions observed in DSC curves (near 110; 175; 250 and 270; and 350 °C) are compared with the melting points of PET oligomers given in the literature [98], it can be attributed that DP is mainly composed of hydroxyl-ended monomer (n = 1); hydroxyl-ended dimer (n = 2) or hydroxyl-carboxyl ended monomer (n = 1); carboxyl-ended oligomers (n = 2, 3, 4); and carboxyl-ended monomer (n = 1), respectively. In addition, other hydroxyl-, hydroxyl-carboxyl, and carboxyl-ended oligomers may also be present in small amounts in the structure. These results indicate that DP is not a pure product but a mixture of PET oligomers [80, 81].

3.3. End-group analyses of DP

In acid value (AV) and hydroxyl value (HV) analyses performed according to related ASTM standards for the characterization of DP, AV and HV of DP were found to be 341 and 186 mg KOH/g, respectively. These values indicate that DP has both hydroxyl and carboxyl end groups. It is seen from both the end-group analysis results and DSC measurements that the raw depolymerization product (DP) obtained from the high-pressure depolymerization of waste PET with DPG and water is a mixture of hydroxyl- and carboxyl-terminated oligomers.

3.4. FTIR and DTA analyses of the alkyds

The FTIR and DTA graphs of AREFT and APET alkyds are given in Figure 5.

Upon examination of the FTIR spectra of AREFT and APETT alkyds (Figure 5a), the stretching vibration ascribed to OH groups is observed as a broad and spread peak around 3500–3460 cm^{-1}. In the 2925–2850 cm^{-1} region, the peaks corresponding to asymmetric and symmetric stretching vibrations of aliphatic C–H groups in the methylene structure (CH_2), are present. A sharp overlapping peak is observed around 1735–1725 cm^{-1} attributed to the stretching vibration of the carbonyl (C=O) groups belonging to the ester and carboxyl groups. In addition, there are peaks assigned to aromatic and aliphatic C=C vibration in the 1600–1575 cm^{-1} region and C–H (CH_2) bending vibration in the 1450–1380 cm^{-1} region. Furthermore, there are peaks belonging to ether C–O–C stretching vibration in the region of 1275–1250 cm^{-1}, aliphatic ester C–O stretching at 1120 cm^{-1}, and aromatic ring C–H in-plane deformation around 1070–1060 cm^{-1}. Additionally, the peaks related to ester C–H out-of-plane bending (985–865 cm^{-1}), and aromatic ring C–H bending and rocking deformation vibrations (785–630 cm^{-1}) are identified in specific regions. All these peaks are typical peaks observed in alkyd resin and ester structures [104–106]. Overall, the FTIR spectra of the synthesized products confirm the formation of the alkyd structure in both the reference resin (AREFT) and the waste PET-based resin (APETT) [99–105].

The melting points of alkyds were determined by DTA analysis. Differential thermal analysis (DTA), like differential scanning calorimetry (DSC), measures the heat input required to increase the temperature of a sample [106]. As seen in the DTA graphs of alkyds given in Figure 5b, the melting temperatures of the reference AREFT and PET-based

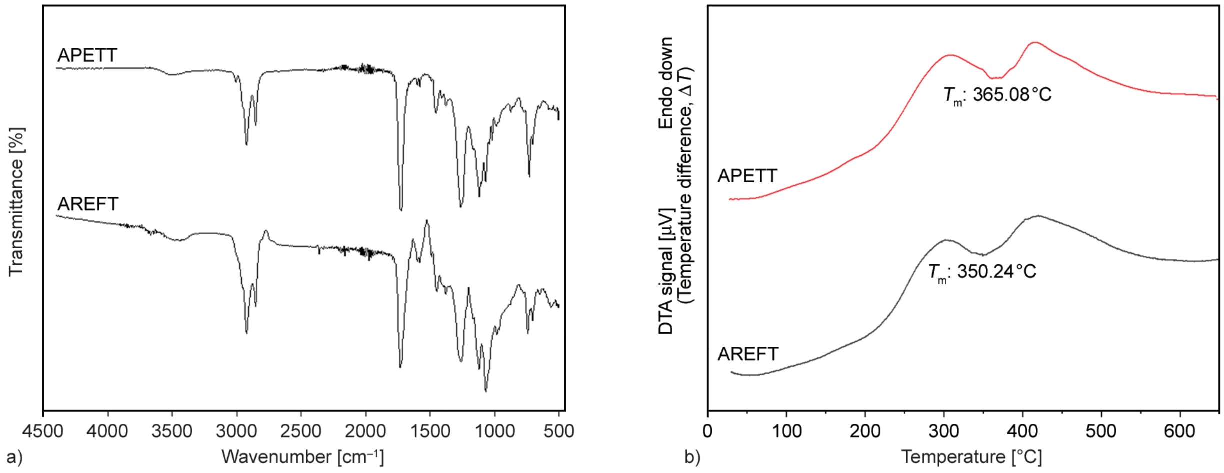

Figure 5. a) FTIR and b) DTA graphs of the alkyds.

APETT alkyds were found to be 350.24 and 365.08 °C, respectively. These values are consistent with the literature [107].

3.5. Rheological properties of the alkyds

The flow behavior of a fluid, including viscosity, is determined by rheological tests. Viscosity is the measure of the internal flow resistance of a fluid, and it refers to how thick a fluid is or how easily it flows [108, 109]. The viscosity of a material can be calculated using the viscosity-flow curves provided by the rheometer. In these viscosity measurements, the flow curves (variation of dynamic/apparent viscosity with shear rate) are determined. When using a rheometer, shear stress and shear rate values are measured over a wide working range, resulting in higher accuracy. Additionally, depending on the system used, only a small sample amount is required for the test [110].

Ideally, viscous flow behavior (Newtonian flow behavior) means that the measured viscosity is independent of the shear rate. If the internal flow resistance of a fluid is independent of the external force (the shear rate) acting upon the fluid, it is ideally viscous and named Newtonian liquid [110, 111]. That is, the viscosity of an ideally viscous (Newtonian) fluid does not change with increasing shear rate and remains constant. In the viscosity graphs shown as dynamic viscosity versus shear rate for Newtonian liquid, the relationship between viscosity and shear rate is observed as a straight line [110].

While ideally, viscous Newtonian fluids have constant viscosity for all shear rate values, on the other hand, for shear-dependent fluids, the viscosity changes with the shear rate. If the viscosity of the fluid changes with the shear rate, it is non-Newtonian fluid and for an exact definition, the apparent viscosity has to be specified. The viscosity in such systems is different at each point on the dynamic viscosity versus shear rate curve. Therefore, it needs to specify at which shear rate a viscosity value was determined. This is the ‘apparent viscosity’ or ‘apparent shear viscosity’. Each apparent value is one point of the viscosity function [112].

Since the resin amounts were insufficient for rotary viscometer measurements, viscosity measurements were performed in a rheometer with a small amount of sample in a very small gap range (1 mm for PP25). Viscosity curves of the reference AREFT alkyd (without PET) and the PET-based APETT alkyd (with PET) obtained from the rheometer are given in Figure 6.

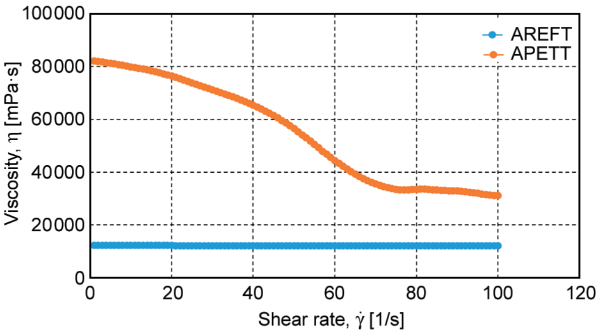

Figure 6. Viscosity-shear rate curves of the alkyds.

As can be seen from Figure 6, AREFT alkyd behaved similarly to the Newtonian liquids. Therefore, the viscosity values depending on the shear rate were averaged. The average viscosity value, η (average), of the AREFT alkyd in measurements by the rheometer was calculated to be 12 122 mPa·s (Table 5). On the other hand, APETT behaved as a non-Newtonian fluid and showed a shear-thinning behavior (pseudoplastic flow behavior) characterized by decreasing viscosity with increasing shear rates. That is, its viscosity decreased with the shear rate. Because the viscosity is shear-dependent, it has to be given with the shear condition. Therefore, only the viscosity values were obtained at specific shear rates (1, 50 and 100 s^{-1}) are presented in Table 5. Since the shear thinning behavior is related to the internal structures of the samples, it is thought that the APETT alkyd exhibits this behavior, probably due to the long oligomer chains incorporated into the structure.

3.6. Other physical properties of alkyds

The acid values of alkyds were performed titrimetrically according to ASTM D-1639 standard. The weight percent nonvolatile (solids) content of alkyds was also determined according to ASTM D7232-06 by loss in weight. Also, the colors of the alkyds were

Table 5. The viscosity measurements of AREFT and APETT resins.

Shear rate [s^{-1}]	AREFT alkyd (Newtonian fluid) Dynamic viscosity [mPa·s]	APETT alkyd (Non-Newtonian fluid) Apparent viscosity [mPa·s]
1	12 226	82 144
50	12 120	56 515
100	12 119	31 098
Average	12 122	–

evaluated visually. The physical properties of synthesized alkyds are given in Table 6.

The viscosity value of the APETT (Table 5), which alkyd synthesized with DP at a ratio of 100% instead of the DPG as a diol component is higher than that of the AREFT alkyd synthesized with DPG as a diol. This result was probably obtained due to incorporating a higher molecular weight DP (PET oligomers mixture) into the alkyd structure. Additionally, as given in Table 6, acid values and solids content percentages of alkyds are close to each other. Moreover, the use of DP did not cause any color change.

3.7. FTIR analyses of ALK-UA and ALK-CHF blends

The FTIR spectra of the ALK-UA blends and ALK-CHF blends in Figure 7.

ALK-UA blends

The characteristic peaks in the UA resin spectrum are as follows (Figure 7a): Stretching vibration of OH groups in the 3625–3330 cm^{-1} region, stretching vibration of C=O bond in ester and aldehyde structures in the 1730–1710 cm^{-1} region, and stretching vibration of C–N bond in amide groups around 1310 cm^{-1} are observed. Peaks belonging to the ester CO bond at 1263 cm^{-1} and stretching vibration of the C=O group in tertiary amide structure at 1640 cm^{-1} are located. Peaks attributed to asymmetric and symmetric stretching vibrations of C–H bonds in CH_3 and CH_2 groups in the 2900–2800 cm^{-1} region and stretching vibrations of C–H bonds in the aldehyde group in the 2750–2500 cm^{-1} region are located. Additionally, peaks belonging to the deformation vibration of C–H bonds in CH_3 and CH_2 groups around 1400 cm^{-1}, symmetric stretching deformation vibration in CH_3 groups around 1300 cm^{-1}, and deformation vibration of methyl groups in the 1200–1100 cm^{-1} region are observed [52, 53, 55].

When the spectra of ALK-AU blends are examined (Figure 7a), it is seen that the peaks belonging to UA resin, alkyds, and blends overlap or interfere, especially in the 1500–800 cm^{-1} region. However, the minor differences observed in the spectra are presented as follows: In the spectra of the ALK-UA blends, a slight decrease was observed in the intensity of the ether C–O–C stretching vibration observed in the 1275–1270 cm^{-1} region in the alkyd structure. On the other hand, the vibration peaks of the aromatic/aliphatic –C=C group observed in the 1600–1575 cm^{-1} region in the spectra of the alkyds have almost disappeared in the spectra of the ALK-UA blends. This situation probably occurs due to the curing/drying reaction occurring over the C=C bonds. Additionally, the tertiary amide carbonyl group (C=O) peak located at 1640–1650 cm^{-1} in the UA resin spectrum occurred as a small peak at 1640 cm^{-1} in both spectrums of the ALK-UA blend. However, the intensity of this peak is not high, probably due to the low amount of UA resin used in the blend structure and the reaction of carbonyl groups. Further, the peaks due to free carboxyl and hydroxyl groups in alkyd resin are observed at 1730 and 1270 cm^{-1}, respectively. The intensity of these peaks slightly decreased, probably due to the cross-linking reactions of free carboxyl and hydroxyl groups of alkyd resin during drying/curing [10]. Moreover, the broad peaks belonging to the –OH stretching vibration of UA resin at approx. 3330 cm^{-1} and the free –OH group of alkyd resin in the region of 3500–3460 cm^{-1} were observed as a broader and flatter peak of about 3600–3500 cm^{-1} in the spectrum of ALK-UA blends. This is probably related to the active role of –OH groups in crosslinking reactions. As a result, these small differences observed in the FTIR spectra, probably due to the low amount of UA resin, may correspond to the possible alkyd and UA reactions that may occur during the chemical drying of ALK-UA blend films by cross-linking.

Alkyd-CHF blends

The characteristic peaks in the CHF resin spectrum are as follows (Figure 7b): –OH stretching vibration originating from hydroxy methyl groups at 3438 cm^{-1}, C–H stretching vibrations of aliphatic CH_2 groups at 2925 cm^{-1}, C=O stretching vibration of the carbonyl group at 1724 cm^{-1}, and peaks attributed

Table 6. The physical properties of long-oil AREFT and APETT resins.

Alkyd resin	Oil length [%]	Diol component	Acid value [mg KOH/g]	Solids content [%]	Color
AREFT	60	Dipropylene glycol (DPG)	15	94	Brown
APETT	60	Depolymerization product (DP)	10	95	Brown

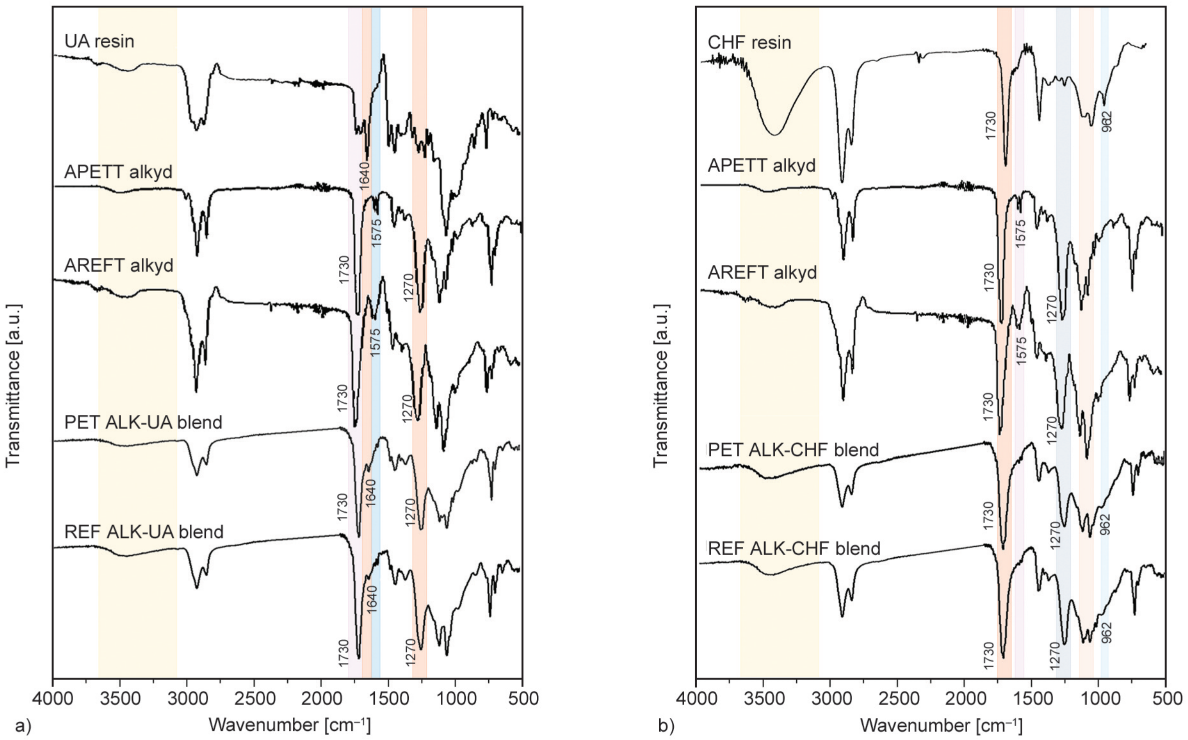

Figure 7. FTIR graphs of the a) ALK-UA and b) ALK-CHF blends.

to methylene bridge at 1450 cm^{-1}. In addition, the peaks belonging to C–O stretching between methylene bridges and cyclic structures found in CHF resin are observed in the 1126–962 cm^{-1} band range [113, 114].

When the spectra of ALK-CHF blends were examined (Figure 7b), the following differences were observed. One of the peaks located in the 1126–962 cm^{-1} band range of the CHF resin spectrum was observed as a small shoulder in the structure of both ALK-CHF blends at 962 cm^{-1}. The others of these peaks around 1100–1050 cm^{-1} overlapped/interfered with the aliphatic ester C–O stretching peaks at 1120 cm^{-1} in the alkyd resin structure. In addition, in the spectra of ALK-CHF blends, a slight decrease is observed in the intensity of the peak attributed to the ether C–O–C stretching vibration at the 1275–1270 cm^{-1} region in the alkyd structure. Further, the vibration peaks ascribed to the aromatic and aliphatic –C=C group in the 1600–1575 cm^{-1} region in the spectra of alkyds almost disappeared in the spectra of ALK-CHF blends. This situation probably appears due to the drying/curing reactions that occur via C=C bonds. Further, the peaks due to free carboxyl and hydroxyl groups in alkyd resin are observed at 1730 and 1270 cm^{-1}, respectively. The intensity of these peaks slightly decreased, probably due to the cross-linking reactions of free carboxyl and hydroxyl groups of alkyd resin during drying/ curing [10]. Moreover, the sharp peak of the –OH stretching vibration of the CHF resin, hydroxyl methyl group located at 3438 cm^{-1} and the spread peak belonging to the alkyd resin free –OH group at the 3500–3460 cm^{-1} region were observed as a single, broad, and wide peak about 3600–3500 cm^{-1} in the spectrum of ALK-CHF blends. This alteration observed in the spectra can probably be attributed to the active role of –OH groups in crosslinking reactions. As a result, these differences observed in the FTIR spectra in the 3650–3000 and 1750–500 cm^{-1} regions probably indicate the reactions that occur during the drying, which, by cross-linking, of the alkyd and CHF resins forming the ALK-CHF blend structure.

3.8. Thermal analyses of ALK-UA and ALK-CHF blends

Thermogravimetric analysis provides practical information on the thermal behavior of polymeric materials and allows their characterization. The weight change of a polymer is measured as a function of temperature and time in a controlled atmosphere [115, 116].

3.8.1. DTG analyses of the blends

Thermal behavior and stability of cured ALK-UA and ALK-CHF blend films were evaluated with data

(TGA and DTG curves) obtained from thermogravimetric analysis in the air atmosphere. As known, the first derivative of the TGA curve (DTG) provides the onset point (initial temperature of peak), midpoint (maximum temperature of peak), and offset point (final temperature of peak) for the decomposition stage and, actually, the onset temperature indicates the thermal stability [117]. According to the literature, the onset point is the initial degradation temperature which corresponds to the intersection of the tangent drawn at the inflection point of the decomposition step with the horizontal zero-line of the TGA curve [118, 119]. The DTG (derivative thermogravimetry) curves derived from TGA (thermogravimetric analysis) data are presented with TGA curves in Figure 8.

As seen in Figure 8, degradation behaviors of both series in the UA-ALK and UA-CHF blends are generally similar, and all blends have one prominent main weight loss step and small step in manner shoulder type or camber. As seen from the DTG curves (the first derivative of the TGA curve), there is a main degradation/decomposition peak in both blend series, giving a maximum (midpoint) of around 290–300 °C (onset point: approx. 220 °C, offset point: approx. 400 °C).

According to the literature, the degradation of alkyd resin has been observed with weight loss occurring between approx. 200 and 400 °C [40]. Previous research reported that the maximum degradation temperature of alkyd resin had been observed at 400 °C, and the weight losses during thermal oxidative degradation of alkyd resins were due to the decomposition of the fatty acid chain and the polyester backbone [40, 120].

In both reference and PET-based series (Figure 8), the alkyd samples without modifier resin (UA = 0 and CHF = 0) showed a degradation behavior with a main peak up to 400 °C observed with an initial temperature of 220 °C (onset point) and a midpoint

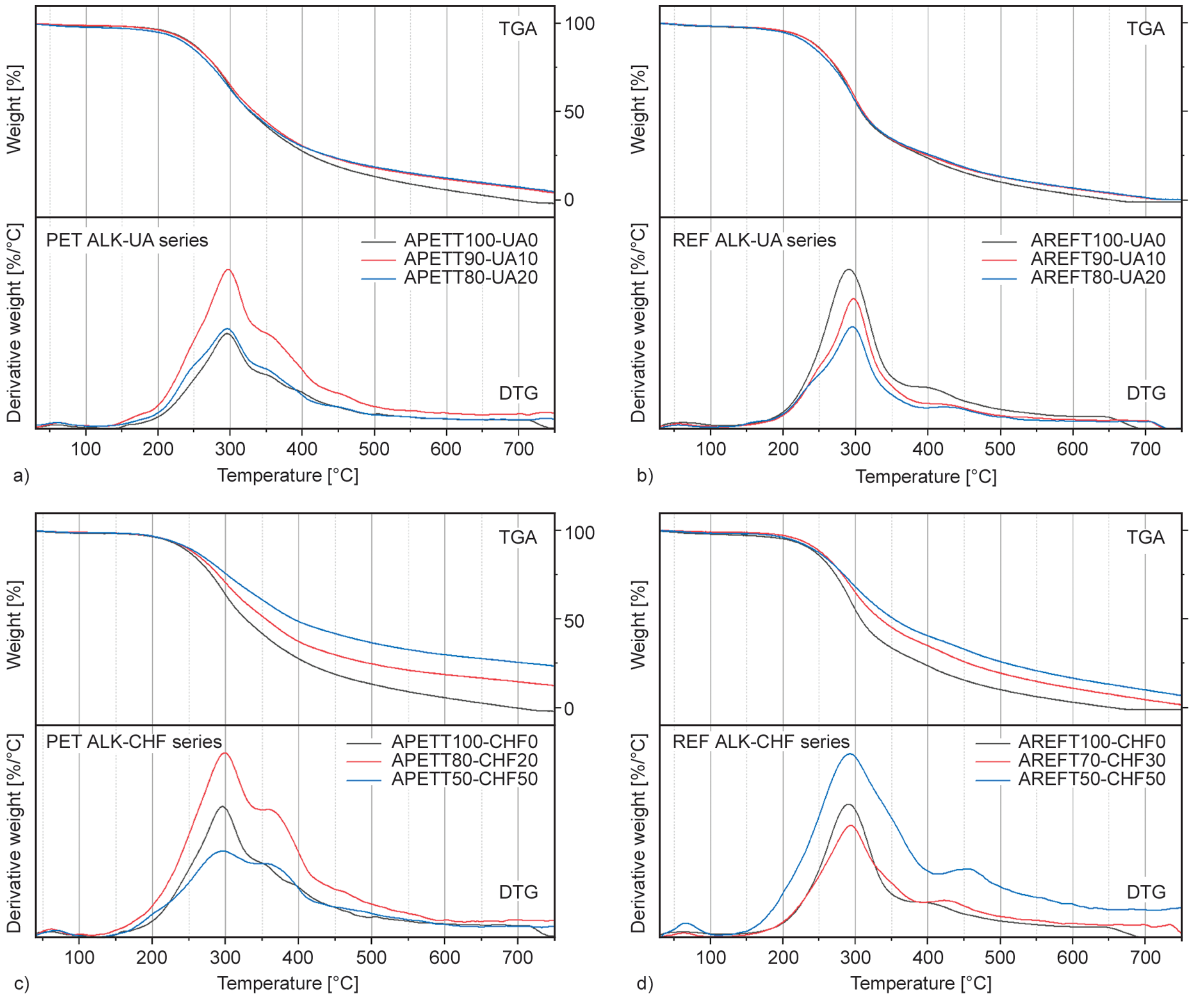

Figure 8. DTG graphs of the blends. a) PET-based ALK-UA blends, b) reference ALK-UA blends, c) PET-based ALK-CHF blends, d) reference ALK-CHF blends.

of 300 °C, consistent with the literature. However, it should also be noted that, generally, the incorporation of PET depolymerization product into the alkyd structure slightly affects the degradation behavior of alkyd resins. As seen in DTG curves, the main weight loss peak of the reference alkyd resin (Figures 8b, 8d) is somewhat sharper, while that of the PET-based resin (Figures 8a, 8c) is wider and not as sharp as those of the reference alkyd. This probably originated from the use of waste PET depolymerization products in the synthesis of the alkyd resin. The weight losses, which are due to PET oligomers about 350–400 °C, are possibly interfering with the main weight loss peak. In addition, in the reference ALK-UA blend series (Figure 8b), the degradation behavior after 400 °C was observed in the manner of small cambers, which may be attributed to modifier (UA) resin in the DTG curves. On the other hand, in the PET-based ALK-UA blend series (Figure 8a), these mentioned cambers, which are thought to be due to the degradation of the small amount of modifying resin (UA) added to the blend, probably interfered with the main weight loss peak observed more broadly due to the presence of PET oligomers in the structure. However, in the case of the ALK-CHF blend series, since the modifier (CHF resin) ratio is higher than those of ALK-UA blend series, mentioned cambers were observed more significantly than in blends containing UA resin, in DTG curves. These mentioned cambers were observed in a manner interfering with the main peak after 350 °C in the PET-based series (Figure 8c) and slightly prominent cambers after 400 °C in the reference series (Figure 8d). Furthermore, the decomposition behavior observed in the ALK-UA and ALK-CHF blend series after 400 °C was probably due to the effect of the aldehyde or ketone resin as a modifier in the blend structure [40, 115, 121].

As a result, we can say that the main weight loss step observed in all blend samples occurred between approx. 220 and 500 °C and continued up to 750 °C. The main weight loss observed between 200 and 400 °C may be due to the decomposition of the alkyd resin. The weight loss observed above 400 °C can be attributed to the decomposition of the cross-linked blend structure containing alkyd and modifier (UA and CHF) resin.

3.8.2. TGA analyses of the blends

To compare the thermal behaviors of the ALK-UA and the ALK-CHF blends with each other, TGA thermograms of all blend films are presented together in Figure 9. In addition, the parameters of TGA analysis are also listed in Table 7.

As seen in Figure 9, the thermal behaviors of the reference and PET-based ALK-UA blends (Figure 9a) are generally similar to each other. The same applies to the reference and PET-based series in the ALK-CHF blends (Figure 9b).

As seen in Table 7, the onset degradation temperatures (onset points) of all ALK-UA and ALK-CHF blends are between 220 and 230 °C and are very close to each other. This indicates that there is no significant difference between the thermal resistances of the blend films at the start. However, as the temperature increased, the weight losses and the thermal oxidative decomposition temperatures and T_{Final} changed. In addition, the residue amounts at the maximum temperature reached by the analysis (800 °C) were also found to be different from each other. Although no difference is observed in onset points, which indicates the thermal resistance/stability, these results may mean that the degradation/decomposition rates or kinetics are different [115, 116]. Additionally, the thermal degradation temperatures at which maximum weight loss (corresponds to midpoints) were observed are between 290–300 °C.

ALK-UA blends

In this series, the thermal degradation temperatures of the PET-based blend films are similar to the reference blend films until 50% weight loss. After this point, in both series, as the amount of UA resin in the blend increased, the thermal degradation temperatures increased slightly after 50% weight loss (Table 7). This increase is probably due to additional cross-linking reactions with the UA resin having hydroxyl groups. In addition, the final thermal oxidative decomposition temperatures of ALK-UA blend series (T_{Final}) observed at the end of the analysis increased in order: AREFT100-UA0 < AREFT90-UA10 < AREFT80-UA20 < APETT100-UA < APETT90-UA10 ≤ APETT80-UA20. The highest T_{Final} value among all ALK-UA blend films was observed in the APETT-UA20 blend film. This increase

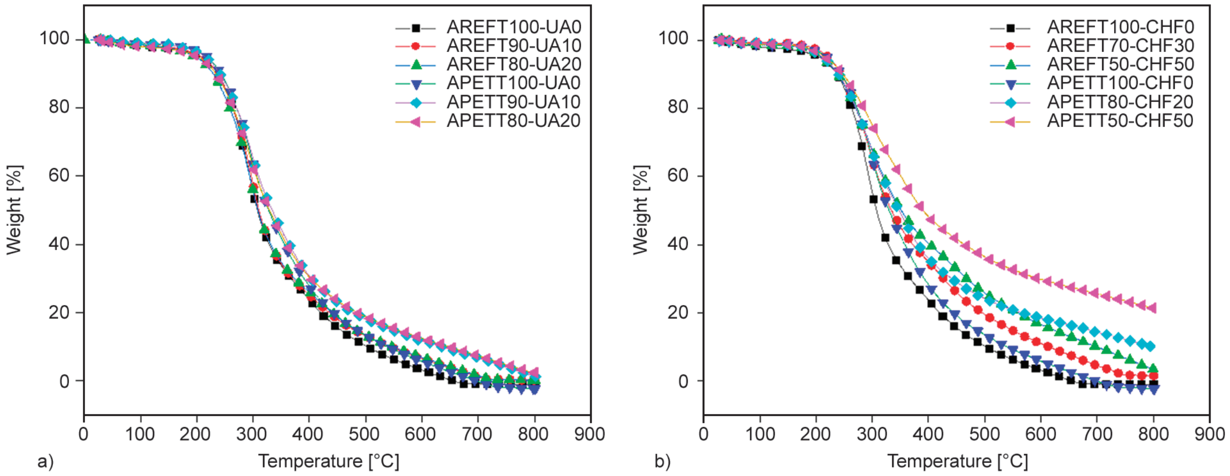

Figure 9. TGA graphs of the a) ALK-UA blends, b) ALK-CHF blends.

observed in the T_{Final} value of the blend is a joint result of using aromatic PET oligomer in alkyd resin synthesis, as well as a physical modification with aldehyde and increasing the amount of UA resin.

Alkyd-CHF blends

In this series, the temperatures corresponding to specific weight loss (for all ratios) in both series are higher than individual alkyd resin (Table 7). That is, a higher temperature is required to achieve the same percentage of matter degradation. Although the degradation onset temperatures have not changed, the changes in the temperatures corresponding to relatively low weight losses, such as 10% can also give us an idea of thermal resistance/stability [122]. In this context, $T_{10\%}$ and $T_{30\%}$ temperatures and the degradation temperatures shown in the TGA curves may mean that the ALK-CHF blend provides higher thermal stability compared to the others (ALK-UA blend, and especially the alone alkyd resin). This thermal stability may be related to the presence of modifier (CHF) in the alkyd structure as it can react by additional cross-linking and contributed cross-linked network.

In ALK-CHF blend series, the thermal degradation temperatures of the PET-based blend films are higher than their counterparts in the reference blend films, starting from 10% weight loss. Long-chain aromatic PET oligomers in the alkyd resin structure in the blend increased thermal degradation temperatures. In both series, as the amount of CHF resin in the blend increases, the thermal degradation temperatures of the blend films also increase. This increase is presumably due to additional cross-linking reactions with the CHF resin. In addition, T_{Final} values increased in order: AREFT100-CHF0 < APETT100-CHF0 < AREFT70-CHF30 < AREFT50-CHF50 ≤ APETT80-CHF20 ≤ APETT50-CHF50. Among all ketone-alkyd blends, APETT50-CHF blend film has the highest T_{Final} value. For this blend, 90% weight loss occurred above 800 °C (weight loss was around 80% at 800 °C). In addition, PET-based ALK-CHF blends containing a ratio of 20 and 50% CHF resin had high residual contents of ~10 and ~20% at 800 °C. In both reference and PET-based blend series, especially when the alkyd resin/CHF resin ratio was 50/50 by weight, the T_{Final} value increased by approx. 1.5 times compared to the alone alkyd resin. As a result, adding CHF resin slightly increased the individual thermal stability of alkyd resin and the thermal resistance of ALK-CHF blends. This increase is a joint result of the use of waste PET product (PET oligomer) in alkyd resin synthesis, physical modification with CHF resin, and increasing the ratio of CHF resin in the blend. Moreover, the residue amounts of the PET-based blends in the maximum temperature reached by the analysis are higher than the reference counterparts. This situation probably occurs due to the using waste PET product (PET oligomer) having aromatic units 100% instead of diol.

In the literature, it has been reported that introducing rigid groups in the main chain, such as double bonds, benzene ring, carbonyl, *etc.,* can improve the thermal stability of the polymer, and the introduction of a cyclic structure on the main chain, conjugated double bonds, or the introduction of large rigid substituents on the side chain will increase the melting point of the molecule [122]. In this context, in the PET-based ALK-CHF blend series, the thermal stability of these alkyd resin-based blends is probably

Table 7. Parameters of TGA analysis of ALK-UA and ALK-CHF blends.

ALK-UA blends	**Onset [°C]**	**Temperatures at specific weight losses [°C]**					**T_{Final}[a] ($T_{100\%}$) [°C]**	**Residue[b] at 800 °C [%]**
		$T_{10\%}$	**$T_{30\%}$**	**$T_{50\%}$**	**$T_{80\%}$**	**$T_{90\%}$**		
Reference blends								
AREFT100-UA0	225	236	280	307	418	501	~670	0
AREFT90-UA10	228	237	292	309	434	542	~700	0
AREFT80-UA20	224	230	278	308	438	545	~740	0
PET-based blends								
APETT100-UA0	227	241	289	327	441	537	~740	0
APETT90-UA10	226	239	291	333	475	633	>800	~1–2
APETT80-UA20	223	233	286	329	484	646	>800	~1–2
ALK-CHF blends	**Onset [°C]**	**Temperatures at specific weight losses [°C]**					**T_{Final}[a] ($T_{100\%}$) [°C]**	**Residue[b] at 800 °C [%]**
		$T_{10\%}$	**$T_{30\%}$**	**$T_{50\%}$**	**$T_{80\%}$**	**$T_{90\%}$**		
Reference blends								
AREFT100-CHF0	225	236	280	307	418	501	~650	0
AREFT70-CHF30	228	245	291	334	495	614	~760	~1–2
AREFT50-CHF50	230	240	296	353	559	701	>800	~3–4
PET-based blends								
APETT100-CHF0	227	241	289	327	441	537	~700	0
APETT80-CHF20	226	247	301	355	572	800	>800	~10–11
APETT50-CHF50	225	250	318	393	800	> 800	>800	~21–22

[a] Final thermo-oxidative degradation temperature,

[b] Residue at the max. temperature reached by the analysis.

increased due to the aromatic ring-containing PET oligomers in the alkyd structure as well as the aromaticity of the CHF resin with benzene ring and its carbonyl content.

As a final word, it is worth noting the following point. In the literature, the use of alkyd, epoxy, acrylic, silicone, and hybrid resins in intumescent/flame retardant coatings has been studied, and these resins have shown promising results for the coatings' intumescence process and in their protection against fire [123–126]. It has previously been reported that resins with higher residual content, such as alkyd, may be advantageous in intumescent coating formulations because they support the formation of a greater residual char layer and increase flame retardancy [123]. There are also studies on the use of modified cyclohexanone-formaldehyde resins in fire-retardant polyurethanes [127] and the production of thermally stable polyurethane foam with ketone-melamine-formaldehyde resin [128]. In this context, it may be tested whether these alkyd-cyclohexanone formaldehyde blends (APETT80-CHF20 and APETT50-CHF50) with higher residue amount can perhaps be included in such coating formulations.

3.9. Drying behaviors of ALK-UA and ALK-CHF blends

The drying behaviors of long-oil ALK-UA and ALK-CHF blends were examined in the air. The drying degrees of all blend films were determined according to the Modified-Bandow-Wolff method (DIN 53150, ISO 9117). The 7th drying degree is the highest value corresponding to the 'full-dry' of this test method. The 'dry-to-touch' stage was determined by the Finger-Touch method (ASTM D 1640).

The drying mechanism of alkyd resins is related to the presence of unsaturated bonds in the oil or fatty acid chains and free functional (hydroxyl and carboxyl) groups in the main and side groups. The drying process occurs as a result of the oxidation of double bonds in the oils or fatty acids by oxygen in the air. This process largely depends on the type of oil or fatty acid and the degree of unsaturation. First, the solvent in the resin structure evaporates (physical drying), and then the resin dries and hardens through reactions which leads to the formation of cross-linked intermolecular bonds via chain polymerization processes (chemical drying) [22, 23, 129, 130]. There are two theories explaining the drying mechanism: peroxide theory and hydroperoxide theory

[130, 131]. According to the peroxide theory, oxygen attaches to the double bond or the methylene groups adjacent to the double bond in the resin structure, leading to the formation of peroxides. These peroxides then bond with another fatty acid, resulting in cross-linking and drying. On the other hand, based on the hydroperoxide theory, oxygen also attaches to the double bond or the methylene groups adjacent to the double bond in the resin structure, causing the formation of hydroperoxides. These hydroperoxides break down into radicals, which then react with other chains to form the cross-linked structure. In the literature, it is noted that air-drying alkyd resins readily form a film through the oxidation of unsaturated groups in their structure with oxygen. In this stage, the presence of carboxyl groups in the alkyd structure accelerates the drying process by helping in hydroperoxide decomposition. Conversely, if the alkyd structure contains more hydroxyl groups, the drying process in the air may slowed down because the hydroxyl groups can make it difficult for hydroperoxide formation to occur. That is, although the excess of hydroxyl groups contributes to the drying process, it may slow down the drying speed in the air [31, 33].

The drying test results of ALK-UA and ALK-CHF blend films are presented in Table 8 and Table 9, respectively. The text below shows the definitions of potential equivalents (drying levels in the tables) in the Finger-Touch method of drying degrees acquired through the Modified-Bandow-Wolff method. *'Dry-to-touch': When the coating is lightly touched by a finger, it does not adhere to the finger. 'Surface-dry': When the coating is pressed strongly with a finger, it moves. 'Dry': When the coating is pressed strongly with a finger, fingerprints form on it. 'Hard-dry': When the coating is pinched by light force between the forefinger and thumb, it is not displaced. 'Through-dry': When the coating is compressed with medium force between the forefinger and thumb, it is not displaced. 'Full-dry': When strong force by a finger is applied to the coating, it does not deteriorate or displace'* [87, 132, 133].

Through-dry and full-dry levels are very close to each other and are difficult to distinguish without using test equipment. The through-dry film is almost completely dry. However, with the cross-linking reactions that continue over time, drying progresses further and reaches the full-dry stage. The full-dry film is fully dry throughout its thickness. Through-dry and full-dry terms are often used interchangeably in the coating industry/technical literature. In fact, it is useful to measure the coatings again several days after they have been thoroughly dry [133].

ALK-UA blends

As seen in Table 8, in general, the drying of the films in both ALK-UA blend series is good in the air. The 'dry-to-touch' stage was reached in 180 min for the films in the reference blend series and in 120 min for the films in the PET-based blend series. These values were obtained as 210 and 150 min for reference alkyd (AREFT100-UA0) and PET-based alkyd (APETT100-UA0) films without UA resin, respectively. As seen in both series, blend films reached the

Table 8. The drying behaviors of ALK-UA blend films.

ALK-UA blends	**Dry-to-touch[a] [min]**	**Drying degree / drying level (Modified-Bandow-Wolff method[b] / possible equivalent of Finger-Touch method)**			
		24 h in the air	**48 h in the air**	**72 h in the air**	**1 h at 130 °C**
Reference blends					
AREFT100-UA0	210	3 / surface-dry	3 / surface-dry	3 / surface-dry	7 / full-dry
AREFT95-UA5	180	3 / surface-dry	3 / surface-dry	3 / surface-dry	7 / full-dry
AREFT90-UA10	180	3 / surface-dry	3 / surface-dry	3 / surface-dry	7 / full-dry
AREFT85-UA15	180	3 / surface-dry	3 / surface-dry	3 / surface-dry	7 / full-dry
AREFT80-UA20	180	3 / surface-dry	3 / surface-dry	3 / surface-dry	7 / full-dry
PET-based blends					
APETT100-UA0	150	5 / hard-dry	6 / through-dry	6 / through-dry	7 / full-dry
APETT95-UA5	120	5 / hard-dry	6 / through-dry	6 / through-dry	7 / full-dry
APETT90-UA10	120	5 / hard-dry	6 / through-dry	6 / through-dry	7 / full-dry
APETT85-UA15	120	5 / hard-dry	6 / through-dry	6 / through-dry	7 / full-dry
APETT80-UA20	120	4 / dry	4 / dry	4 / dry	7 / full-dry

[a] According to Finger-Touch method,
[b] The 7th drying degree is the highest value of this test method.

'dry-to-touch' stage faster than individual alkyd films, which shows the positive contribution of UA resin to the drying of alkyd resin. This is probably due to the UA resin with hydroxyl groups causing additional cross-linking reactions, thus promoting drying reactions. However, the further drying of the films in the reference ALK-UA blend series progressed relatively slowly in the air. Although they reached the 'dry-to-touch' stage in 180 min, they remained at the 3rd drying degree, probably corresponding to a 'surface-dry' level, after 72 h in the air. On the other hand, the further drying of the films in the PET-based ALK-UA blend series progressed faster than their reference counterparts. This shows the positive contribution of the waste PET depolymerization product to the drying process. The PET-based blend films that reached the 'dry-to-touch' stage in 120 min, achieved the 5th drying degree, probably corresponding to a 'hard-dry' level after 24 h, in the air. At the end of 72 h, they arrived at the 6th drying degree, probably corresponding to a 'through-dry' level in the air. This situation is likely due to the presence of depolymerization products (DP) containing oligomers with hydroxyl and carboxyl end groups in the resin structure. Nevertheless, in the PET-based blend series, when UA resin was used at a ratio of 20%, it decreased the drying speed a bit. This result showed that the appropriate ratio for UA resin in the blend structure should be up to a maximum 15% in terms of drying features. To accelerate the drying process and to ensure complete drying (for the 7th drying degree), all ALK-UA blend films were oven-cured at 130 °C for 1 h. At the end of the oven-curing, all blend films reached the 7th drying degree, signifying the full-dry stage. Then, all physical and chemical surface coating tests were applied to fully dry films.

ALK-CHF blends

As seen in Table 9, in general, the drying of the films in both ALK-CHF blend series is good in the air. The 'dry-to-touch' stage was reached in 45 to 180 min for the films in the reference blend series, and 30 to 60 min for the films in the PET-based blend series. These values were obtained as 210 and 150 min for reference alkyd (AREFT100-CHF0) and PET-based alkyd (APETT100-CHF0) films without CHF resin, respectively. As seen in both series, blend films reached the 'dry-to-touch' stage much faster than individual alkyd films. In both blend series, an increase in the amount of CHF resin resulted in a much higher initial drying speed. When the CHF resin was used at a ratio of 40% (and above) for the reference series, and 20% (and above) for the PET-based series, the films reached the 'dry to touch' stage more quickly. This situation shows the significant contribution of the presence of the CHF resin to the drying process. In both series, it is observed that the further drying process of the ALK-CHF blend films is accelerated with the incorporation of CHF resin into the alkyd structure. While, the dryness of reference alkyd film is 3rd drying degree (probably surface-dry) and the PET-based alkyd film is 5th drying degree (probably hard-dry) after 24 h, with the addition of a ratio at 20% CHF resin, reference and PET-based blend

Table 9. The drying behaviors of ALK-CHF blend films.

ALK-CHF blends	**Dry-to-touch[a] [min]**	**Drying degree / drying level (Modified-Bandow-Wolff method[b] / possible equivalent of Finger-Touch method)**			
		24 h in the air	**48 h in the air**	**72 h in the air**	**1 h at 130°C**
Reference blends					
AREFT100-CHF0	210	3 / surface-dry	3 / surface-dry	3 / surface-dry	7 / full-dry
AREFT80-CHF20	180	4 / dry	4 / dry	4 / dry	7 / full-dry
AREFT70-CHF30	180	4 / dry	4 / dry	4 / dry	7 / full-dry
AREFT60-CHF40	60	4 / dry	4 / dry	4 / dry	7 / full-dry
AREFT50-CHF50	45	4 / dry	4 / dry	4 / dry	7 / full-dry
PET-based blends					
APETT100-CHF0	150	5 / hard-dry	6 / through-dry	6 / through-dry	7 / full-dry
APETT80-CHF20	60	6 / through-dry	6 / through-dry	6 / through-dry	7 / full-dry
APETT70-CHF30	60	6 / through-dry	6 / through-dry	6 / through-dry	7 / full-dry
APETT60-CHF40	30	6 / through-dry	6 / through-dry	6 / through-dry	7 / full-dry
APETT50-CHF50	30	6 / through-dry	6 / through-dry	6 / through-dry	7 / full-dry

[a] According to Finger-Touch method,˙

[b] The 7th drying degree is the highest value of this test method.

films reached the 4th drying degree (probably dry) and 6th drying degree (probably through-dry), respectively. This situation shows the positive contribution of the CHF resin addition to the drying speed of alkyd resin. The presence of CHF resin probably caused additional crosslinking reactions due to the carbonyl group in the resin structure. As given in the literature, CHF resin facilitates oxidative drying by activating the methylene groups in the alkyd resin structure, thereby accelerating the drying process [48, 50]. Additionally, the films without PET in the reference ALK-CHF blend series achieved the 4th drying degree, which may correspond to a 'dry' level, after 24 h in the air. On the other hand, at the end of 24 h, the films in the PET-based blend series arrived at the 6th drying degree, which may correspond to a 'through-dry' level, in the air. As can be seen, in the ALK-CHF blend series, the drying rate of the PET-based blend films is higher than their reference counterparts. These PET-based films are almost completely dry after 24 h. This situation is probably a result of the use of the depolymerization product (DP) consisting of mixtures of hydroxyl and carboxyl functional oligomers that could cause additional crosslinking reactions, and the use of DP affected the drying process. In conclusion, both the use of DP and the addition of CHF resin positively contributed to the drying process. To accelerate drying and to ensure complete drying (for the 7th drying degree), all ALK-CHF blend films were oven-cured at 130 °C for 1 h to achieve complete drying and reach the 7th drying degree. Complete drying occurred at all ratios after curing in both blend series.

Comparison of drying behavior of ALK-UA and ALK-CHF blends

The drying degrees of ALK-UA and ALK-CHF resins are presented together in Figure 10 for comparison.

As seen in Figure 10, adding UA or CHF resin to alkyd resin shortened the 'dry-to-touch' time in both blend series. However, when UA resin was used, this effect did not change depending on the resin ratio and remained constant. In ALK-UA blends, no impact of DP use was also observed at this time. In the case of the ALK-CHF blends, the 'dry-to-touch' time decreased significantly with the adding CHF resin compared to the alkyd resin. Moreover, as the CHF resin ratio increased, the films reached this level more quickly. In ALK-CHF blends, this effect was also observed more in the case of DP use. Among ALK-UA and ALK-CHF blends, the shortest time to reach the 'dry-to-touch' stage was observed in the reference and PET-based blend films (45 and 30 min) containing a 50% CHF resin ratio. The modifier resins added to the blend structure and the depolymerization product included in the alkyd formulation probably accelerated the drying mechanism by additional possible crosslinking reactions mentioned above.

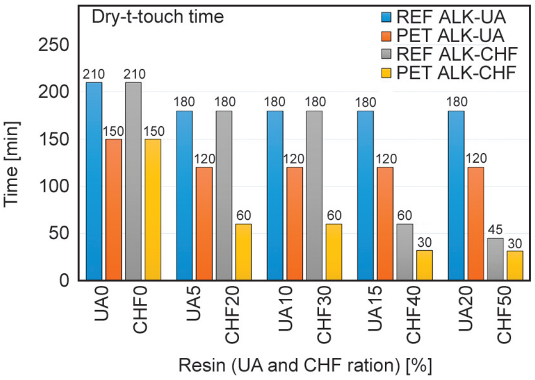

Figure 10. Dry-to-touch time of the blends.

3.10. Physical coating properties of ALK-UA and ALK-CHF blends

To determine the physical coating properties, all tests were applied according to related standards using coating instruments on oven-cured (full-dry) films. Two samples were used to obtain repeatable results.

ALK-UA blends

The physical coating test results of ALK-UA blend films are presented in Table 10, and the results presented in this table were evaluated in detail below, one by one.

Hardness

The damping-off (a decrease in the amplitude of an oscillation) time of the König pendulum on the standard glass test surface (the hardest material for this test) is 250±10 s [134]. As seen in Table 10, the hardness of the films prepared from ALK-UA blends is generally good, and medium-hard (80–84 and 73, 79, 85, 112 König s) and hard (127–135 König s) films were obtained. In both series, when the UA resin is used at a ratio of 15% and above, UA resin contributes to hardness values, and the hardness of the alone alkyd resin (78 and 66 König s) significantly increases. This increase was observed more clearly in the reference series at 15 and 20% UA resin ratios (127 and 135 König s) and in the PET-based series at 20% UA resin ratios (112 König s). The increase in hardness value is probably due to additional cross-linking reactions with the hydroxyl-terminated UA resin used as a modifier. However, according to experimental results, it is understood that the UA resin ratio should be at an optimum value of 15–20% to observe this effect. Additionally, in the reference and PET-based ALK-UA blend series, the hardness values of the films are close to each other. That is, there was no positive or negative effect of using waste PET products (DP).

Adhesion

A value of 100% corresponds to excellent adhesion strength according to the used standard. As seen in Table 10, the adhesion test results of films in the reference and PET-based ALK-UA blend series are 100%, and all of them show excellent adhesion and scratch resistance. According to these results, it appears that the use of waste PET product (DP) and blending with UA resin does not have a negative effect on the adhesion property.

Abrasion resistance

When the abrasion resistance values of the films in the reference and PET-based ALK-UA blend series are examined (Table 10), it is observed that as the amount of UA resin in the blend increases, their abrasion resistance decreases slightly. Abrasive resistance is a combination of basic factors such as elasticity, hardness, strength, toughness, and thickness, and since coatings with flexible networks can disperse the impact stress, they provide better abrasion resistance [135, 136]. Therefore, the abrasion resistance test can give an idea about both the abrasion and flexibility properties of the films. In this context, the abrasion resistance of rigid and non-flexible films probably decreases inversely with hardness. Consistent with this approach, the abrasion resistance of blend films decreased as their hardness increased [37]. Using more amount modifier UA resin increases the hardness through additional cross-linking reactions in the blend structure, resulting in more rigid films being obtained. In addition, the films in the PET-based blend series have slightly higher abrasion resistance values than those of the reference blend series. Abrasion resistance is a feature that gives an idea about the flexibility of films, as mentioned above. Hard films can be expected to have low flexibility, soft films to have high flexibility, and films with similar hardness values can be expected to have similar abrasion resistance. However, the abrasion resistance values of the films in the PET-based and reference blend series, which have parallel hardness values, are not at the same level. This situation probably originated from the long-chain oligomeric structures (PET oligomers) in the APETT-UA blend structure. In both blend series, the increase in the amount of UA resin reduces the abrasion resistance. On the other hand, at the same time, in the PET-based blend series, the oligomeric long chains in the structure increase flexibility, resulting in increased abrasion resistance. The difference in abrasion resistance level observed in the reference and PET-based blend series probably arises due to the joint effect of these two factors.

Impact resistance

The maximum value measured by the impact tester that complies with this standard is 200 kg·cm. The

Table 10. The physical surface coating test results of ALK-UA blend films.

ALK-UA blends	Hardness [König s]	Adhesion strength [%]	Abrasion resistance [mL sand]	Impact resistance [kg·cm]	Gloss at 60° [Gloss unit, GU]
Reference blends					
AREFT100-UA0	78	100	1600	>200	143
AREFT95-UA5	80	100	650	>200	144
AREFT90-UA10	84	100	600	>200	145
AREFT85-UA15	127	100	500	>200	147
AREFT80-UA20	135	100	450	>200	148
PET-based blends					
APETT100-UA0	66	100	1600	>200	88
APETT95-UA5	73	100	1300	>200	91
APETT90-UA10	79	100	1200	>200	94
APETT85-UA15	85	100	850	>200	96
APETT80-UA20	112	100	800	>200	98

impact resistance values of medium hard and hard films in the reference and PET-based ALK-UA blend series were found to be >200 kg·cm and their impact resistances were excellent (Table 10). The use of waste PET product (DP) and modification with UA resin did not have a negative effect on the impact resistance.

Gloss

According to standards about gloss, values higher than 80–85 GU at 60° correspond to very gloss coatings [137]. As seen in Table 10, very gloss films were obtained from reference ALK-UA blends, while gloss films were obtained from PET-based ALK-UA blends. In the PET-based blend series, gloss values were lower than those in the reference blend series. It is thought that this may be due to the oligomeric structures on the PET-based alkyd resins in the blend structure. However, in both blend series, as the amount of UA resin in the blend increased, the gloss increased slightly.

ALK-CHF blends

The physical coating test results of ALK-CHF blend films are presented in Table 11, and the results presented in this table were evaluated in detail below, one by one.

As seen in Table 11, in general, medium hard/hard and gloss films having excellent adhesion, relatively flexible, and excellent impact resistance were obtained from reference and waste PET-based ALK-CHF blends.

Hardness

The hardness of the films in the reference and PET-based ALK-CHF blend series is generally good, and medium hard (97–109 and 93, 102, 104, 106 König s) and hard (128–140 König s) films were obtained (Table 11). In both series, adding CHF resin to the blend structure improved the hardness values of the films, and the hardness of the alone alkyd resin (78 and 66 König s) significantly increased. Moreover, as the CHF resin ratio in the blend increased, the hardness values increased in parallel. This increase is probably related to the contribution of CHF resin to cross-linking reactions.

As known, the drying mechanism of alkyd resins is related to the presence of unsaturated bonds in the fatty acid chains and free functional (hydroxyl, carboxyl, methylene) groups in the main and side groups. Alkyd resins dry and harden through reactions between unsaturated bonds and hydroxyl groups, leading to the formation of cross-linked intermolecular bonds via chain polymerization processes [138]. In addition, as given in the literature, CHF resin promotes the formation of more cross-linked networks, which leads to higher hardness in the cross-linked structures [48, 50]. This effect has been attributed to the Michael-Russell mechanism, which supports network formation in the alkyd coating in the literature [48, 139, 140]. Moreover, all cross-linking reactions that can be caused by the oxygen activation of the methylene group [48], the reactions of free hydroxyl and/or carboxyl groups [10, 22, 138], and the presence of carbonyl groups in

Table 11. The physical surface coating test results of ALK-CHF blend films.

ALK-CHF blends	Hardness [König s]	Adhesion strength [%]	Abrasion resistance [mL sand]	Impact resistance [kg·cm]	Gloss at 60° [Gloss unit, GU]
Reference blends					
AREFT100-CHF0	78	100	1600	>200	143
AREFT80-CHF20	97	100	1400	>200	140
AREFT70-CHF30	109	100	1250	>200	139
AREFT60-CHF40	128	100	700	>200	139
AREFT50-CHF50	140	100	500	>200	139
PET-based blends					
APETT100-CHF0	66	100	1600	>200	88
APETT80-CHF20	93	100	1450	>200	105
APETT70-CHF30	102	100	1250	>200	102
APETT60-CHF40	104	100	1250	>200	98
APETT50-CHF50	106	100	900	>200	90

CHF resin [48, 50] are probably simultaneously effective in the drying process of the ALK-CHF blend films. As a result, this joint effect probably led to a more extensively cross-linked network (high cross-linked density), resulting in a harder and more compact structure here. However, the hardness values of reference ALK-CHF blend films are slightly higher than those of PET-based ALK-CHF blends. This situation is probably caused by the presence of longer chain oligomeric structures (DP) that may cause flexibility in blends containing waste PET-based alkyd resin. In the reference ALK-CHF blend series, the increase in hardness values is prominently observed in all films, and the hardness value increases up to 140 König s. In this series, as the amount of CHF resin increased, the hardness value gradually increased. On the other hand, in the PET-based ALK-CHF series, hardness increased significantly in blends containing 20 and 30% ratio of CHF resin compared to the blend without CHF resin (alkyd resin). When the CHF resin was added at ratios of 40 and 50%, the hardness values did not change much and remained at almost a similar level as the blend containing a 30% ratio of CHF resin. That is, the use of the CHF resin above 30% did not have a significant effect on the hardness, which may be related to the use of DP, as mentioned above. According to the experimental results, it is understood that the modifying with CHF resin should be at an optimum ratio of 30% to observe its positive effect on the hardness of the PET-based ALK-CHF blend series.

Adhesion

The adhesion test results of the films in the reference and PET-based ALK-CHF blend series were 100%, and all of them showed excellent adhesion strength and scratch resistance (Table 11). According to these results, it is seen that the use of waste PET product (DP) and modification with CHF resin does not have a negative effect on the adhesion property of ALK-CHF blends.

Abrasion resistance

In both reference and PET-based ALK-CHF blend series, it is observed that as the amount of CHF resin increases, the abrasion resistance decreases (Table 11). Abrasion resistance values changed inversely proportional to hardness values, and as hardness increased, abrasion resistance decreased. Using less amount of modifier CHF resin probably resulted in more flexible films due to less cross-linking density. In addition, in both series, the observed decrease in abrasive resistance at higher CHF resin additions than 30% (40 and 50%) can probably related to the fact that 30% is the optimum ratio for CHF resin according to experimental results. This was also stated in the section on hardness values.

Impact resistance

The impact resistance values of medium hard and hard films in the reference and PET-based ALK-CHF blend series are determined as >200 kg·cm (Table 11). All films in both series have excellent impact resistance. The presence of waste PET product (DP) in the blend structure and modification with CHF resin did not have a negative effect on the impact resistance of blend films.

Gloss

As seen in Table 11, very gloss (139–140 GU) films were obtained in the reference ALK-CHF blend series, while gloss (90–105 GU) films were obtained in the PET-based ALK-CHF blend series. The gloss values of all blend films in the reference ALK-CHF blend series are at the same level as the alone alkyd resin film (143 GU). In this case, for the reference blend series, it can be said that the addition of CHF resin does not have a negative or positive effect on the gloss. However, in the PET-based ALK-CHF blend series, the gloss values of all blend films were found to be higher than the film alone alkyd resin film (88 GU). The addition of CHF resin increased the gloss of the alkyd resin. That is, for the PET-based blend series, the presence of CHF resin has a positive effect on gloss.

Additionally, PET-based ALK-CHF blend series, the gloss value of the film alone alkyd (without CHF resin) (88 GU) is lower than the reference equivalent (143 GU). This is probably due to the oligomeric structures (DP) in the PET-based alkyd structure. Moreover, it is seen that the gloss values of all blend films with CHF resin in this series are also lower than their counterparts in the reference blend series. In the PET-based blend series, the oligomeric long chains in the structure reduced the gloss, while at the same time, increasing the amount of CHF resin seems to increase the gloss. The difference observed in the gloss values in the reference and PET-based ALK-CHF blend series is probably due to the joint effect of PET oligomers and CHF resin in the structure.

3.11. Chemical coating properties of ALK-UA and ALK-CHF blends

To determine the chemical coating properties, all tests were applied according to related standards and literature on oven-cured (full-dry) films. Two samples were used to obtain repeatable results.

ALK-UA blends

Alkali, acid, salt and water resistance test results of ALK-UA blend films are presented in Table 12. In addition, solvent and environmental resistance test results were also presented in Table 13. The results presented in these tables were evaluated in detail below, one by one.

Alkali resistance

The alkali resistance of alkyd resins is generally considered poor due to the presence of hydrolysable ester bonds [141], and this feature is generally developed with various modifications for many applications. As seen in Table 12, the alkali resistance of the films in the reference ALK-UA blend series is poor. However, in this blend series, it was observed that the alkali resistance of the films containing UA resin at the ratio of 15 and 20% increased slightly, and the films resisted dilute alkali solution for 2 h. This result shows the positive contribution of UA resin to the alkali resistance of blends, and according to experimental results, at least 15% of UA resin must be used for this contribution to occur. On the other hand, it can be seen that all of the films in the PET-based ALK-UA blend series resisted the dilute alkali solution for more than 72 h. In the synthesis of the alkyd resin in blend structure, the use of a longer-chain waste PET oligomer mixture instead of the diol component increased its alkali resistance. When the alkali resistance test was repeated with concentrated alkali solution (3 wt% NaOH) for PET-based ALK-UA blend series, it was seen that the films of alone alkyd resin (without UA resin) and blend with 5% UA resin resisted the alkali solution for 24 h. Moreover, when the UA resin ratio in the blend is increased to 10% or more, the durability period reaches 48 h. Here, the hydroxyl-terminated UA resin which causes possible additional cross-linking reactions, as well as the addition of longer-chain PET oligomer instead of the diol component to the alkyd structure made a positive contribution to the alkali resistance.

As known, various modifications can be done to improve the weak alkali resistance of alkyd resins. In general, when the results regarding alkali resistance are evaluated collectively, it can be said that alkali resistance slightly increased with the use of waste PET products and UA resin modification. Especially for PET-based blend films in the ALK-UA series, where the UA resin ratio is 10% and above, alkali resistance is good compared to the literature.

Acid, salt, and water resistance

All the films in the reference and PET-based ALK-UA blend series were not affected in any way by corrosive ambient conditions such as concentrated acid and salt solutions after 72 h and water after 18 h (Table 12). The films in both blend series have

Table 12. The chemical surface coating test results of ALK-UA blend films.

ALK-UA blends	**Alkali resistance 0.1 M NaOH**	**Alkali resistance 3 wt% NaOH**	**Acid resistance 3 wt% H_2SO_4 72 h**	**Salt resistance 5 wt% NaCl 72 h**	**Water resistance Distilled water 18 h**
	Time of separation of the film from the surface				
Reference blends					
AREFT100-UA0	30 min	-	NA	NA	NA
AREFT95-UA5	30 min	–	NA	NA	NA
AREFT90-UA10	30 min	–	NA	NA	NA
AREFT85-UA15	2 h	–	NA	NA	NA
AREFT80-UA20	2 h	–	NA	NA	NA
PET-based blends					
APETT100-UA0	>72 h	24 h	NA	NA	NA
APETT95-UA5	>72 h	24 h	NA	NA	NA
APETT90-UA10	>72 h	48 h	NA	NA	NA
APETT85-UA15	>72 h	48 h	NA	NA	NA
APETT80-UA20	>72 h	48 h	NA	NA	NA

NA: not affected

excellent acid, salt, and water resistance. The use of waste PET products and modification with UA resin did not have a negative effect on acid, salt, and water resistance.

Solvent resistance

The films in the reference and PET-based ALK-UA blend series were not affected by methanol, toluene, and ethyl acetate, but were slightly affected by acetone (Table 13). Additionally, when counterpart alkyd films (alone alkyd without UA resin) in the reference and PET-based blend series were compared with each other, it was observed that the reference alkyd film was affected by acetone, whereas the PET-based alkyd film was not affected due to the presence of waste PET product. However, the films in the PET-based blends series also started to be affected by acetone after adding a 10% ratio of UA resin. This is related to the wide solubility of UA resin in various solvents.

Environmental resistance

All films in the reference and PET-based ALK-UA blend series were not affected by environmental conditions after 10 cycles (Table 13). No deformation on the blend films was observed in this accelerated ambient test, in which changing ambient/climate conditions were rapidly simulated with wet-cold-dry-heating repetitions. Films in both blend series showed excellent environmental resistance.

ALK-CHF blends

Alkali, acid, salt and water resistance test results of ALK-CHF blend films are presented in Table 14. In addition, solvent and environmental resistance test results were also presented in Table 15. The results presented in these tables were evaluated in detail below, one by one.

Alkali resistance

In general, the films in the reference ALK-CHF blend series were affected by diluted alkali solution (Table 14). However, in this blend series, as the CHF resin ratio increased, the alkali resistance of the blend films gradually increased significantly. The reference alkyd film (alone alkyd without CHF resin) resisted the alkali solution for a maximum of 30 min. On the other hand, while the reference blend film with a 30% ratio of CHF resin resisted for 6 h, the blend films with a 40% ratio and 50% of CHF resin resisted for 24 and 48 h, respectively. These results show the positive contribution of CHF resin to the alkali resistance of the individual alkyd resin and the reference ALK-CHF blend. According to experimental results, this contribution is observed more clearly when 50% CHF resin is used. Moreover, the films in the PET-based ALK-CHF blend series are much more durable than the reference blend series, and all films in this series withstood diluted alkali solution for more than 72 h. The addition of a longer-chain waste PET product (oligomer mixture) to the alkyd structure instead

Table 13. The solvent and the environmental resistance test results of ALK-UA blend films.

ALK-UA blends	Solvent resistance				Environmental resistance (10 cycles)
	Acetone	Toluene	Methanol	Ethyl acetate	
Reference blends					
AREFT100-UA0	S	NA	NA	NA	NA
AREFT95-UA5	S	NA	NA	NA	NA
AREFT90-UA10	SS	NA	NA	NA	NA
AREFT85-UA15	SS	NA	NA	NA	NA
AREFT80-UA20	T	NA	NA	NA	NA
PET-based blends					
APETT100-UA0	NA	NA	NA	NA	NA
APETT95-UA5	NA	NA	NA	NA	NA
APETT90-UA10	S	NA	NA	NA	NA
APETT85-UA15	S	NA	NA	NA	NA
APETT80-UA20	S	NA	NA	NA	NA

NA: not affected,
S: the film shrunk,
SS: the film slightly shrunk,
T: the trace was formed in the film.

Table 14. The chemical surface coating test results of ALK-CHF blend films.

ALK-CHF blends	Alkali resistance 0.1 M NaOH	Alkali resistance 3 wt% NaOH	Acid resistance 3 wt% H_2SO_4 72 h	Salt resistance 5 wt% NaCl 72 h	Water resistance Distilled water 18 h
	Time of separation of the film from the surface				
Reference blends					
AREFT100-CHF0	30 min	–	NA	NA	NA
AREFT80-CHF20	45 min	–	NA	NA	NA
AREFT70-CHF30	6 h	–	NA	NA	NA
AREFT60-CHF40	24 h	–	NA	NA	NA
AREFT50-CHF50	48 h	–	NA	NA	NA
PET-based blends					
APETT100-CHF0	>72 h	24 h	NA	NA	NA
APETT80-CHF20	>72 h	24 h	NA	NA	NA
APETT70-CHF30	>72 h	48 h	NA	NA	NA
APETT60-CHF40	>72 h	48 h	NA	NA	NA
APETT50-CHF50	>72 h	72 h	NA	NA	NA

NA: not affected

of the diol component probably increased the alkali resistance of the ALK-CHF blend.

The alkali resistance properties of the films in the PET-based ALK-CHF blend series were tested again using a concentrated alkali (3 wt% NaOH) solution. The films in the PET-based blend series, which do not contain CHF resin (alone alkyd resin) and contain a 20% ratio of CHF resin, resisted alkali solution for 24 h. Furthermore, when the modifier CHF resin ratio in the blend is increased to 30 and 40%, the durability period reaches 48 h, and at 50%, it reaches 72 h. Both the use of longer-chain PET oligomers (DP) instead of the diol component in the alkyd structure and the addition of CHF resin, which causes possible cross-linking reactions, have a positive contribution to alkali resistance. As a result, when all results of the alkali resistance tests are evaluated together, it is seen that the use of waste PET product (DP) and modification with CHF resin significantly improved the individual alkali resistance of alkyd resins and increased the duration of endurance of ALK-CHF blends to alkali solution (>72 h).

Acid, salt, and water resistance

All the films in the reference and PET-based ALK-CHF blend series were not affected in any way during acid, salt, and water resistance tests (Table 14). None of the films was deformed, their shapes and appearances/colors did not change with corrosive conditions such as concentrated sulfate acid and concentrated aqueous sodium chloride solutions after 72 h and water after 18 h during acid, salt, and water resistance tests. As a result, films in both blend series have excellent acid, salt, and water resistance. The use of waste PET products and modification with CHF resin did not have a negative effect on these properties.

Solvent resistance

All films in the reference and PET-based ALK-CHF blend series were not affected by methanol, toluene, and ethyl acetate, but were slightly affected (shrunk) by acetone. This is related to the wide solubility of CHF resin in various solvents. However, only one blend film based on waste PET and containing a 50% ratio of CHF resin (APETT50-CHF50) was not affected by any solvent (Table 15). These results show the positive contribution of CHF resin and DP to the solvent resistance of the blend, probably due to increased cross-linking. According to experimental results, in the PET-based ALK-CHF blend series, to observe this contribution, CHF resin should be used at an optimum ratio of 50%.

Environmental resistance

None of the films in the reference and PET-based ALK-CHF blend series was affected by environmental conditions after 10 cycles, in which changing ambient conditions were rapidly simulated (Table 15). All ALK-CHF blend films in both blend series showed excellent environmental resistance.

Table 15. The solvent and the environmental resistance test results of ALK-CHF blend films.

ALK-CHF blends	Solvent resistance				Environmental resistance (10 cycles)
	Acetone	Toluene	Methanol	Ethyl acetate	
Reference blends					
AREFT100-CHF0	S	NA	NA	NA	NA
AREFT80-CHF20	S	NA	NA	NA	NA
AREFT70-CHF30	S	NA	NA	NA	NA
AREFT60-CHF40	S	NA	NA	NA	NA
AREFT50-CHF50	S	NA	NA	NA	NA
PET-based blends					
APETT100-CHF0	S	NA	NA	NA	NA
APETT80-CHF20	S	NA	NA	NA	NA
APETT70-CHF30	S	NA	NA	NA	NA
APETT60-CHF40	S	NA	NA	NA	NA
APETT50-CHF50	NA	NA	NA	NA	NA

NA: not affected,
S: the film shrunk.

3.12. Comparison with the literature

No new and recent similar study of this type has been found on ALK-UA and ALK-CHF combinations. Additionally, there are no test results that are directly comparable to coating properties of ALK-UA blends in the few alkyd/aldehyde combinations in the literature. However, the results of this study are summarized comparatively with the few existing similar studies in the tables below. The physical/chemical coating properties and thermal properties of the alkyd-aldehyde and alkyd-ketone combinations in the literature were presented in Table 16 and Table 17.

When comparing the physical coating properties of ALK-UA and ALK-CHF blends with similar studies in the literature (Table 16), we obtained harder, glossier, and higher impact resistance films with excellent adhesion. Additionally, the dry-to-touch times of the blend films were comparable to those found in the literature. Moreover, the PET-based ALK-CHF blend films at a ratio of 40 and 50% CHF resin reached the dry-to-touch stage in a shorter time (30 min) than similar combinations in the literature. This feature is a desired and preferred property for coatings. When the chemical coating results of the blends were compared to the literature (Table 17), we obtained films with higher alkali, acid, and water resistance, withstand corrosive conditions, and have excellent environmental resistance.

In addition, when all results of this study are compared with the alkyd-melamine-ketone systems (ALK-MF/CHF blends) prepared in our recent study [68] (not given in the tables), it is seen that the abrasion and impact resistance values of ALK-UA and ALK-CHF blends prepared with long-oil TOFA-alkyd in this study are higher than the alkyd-MF/CHF blends prepared with short-oil COFA-alkyd (COFA: coconut oil fatty acid) in our other study (impact: 50, 75, 100 kg·m, abrasion: 250, 300, 450 mL sand). This situation is probably due to the high cross-linking ratio in the oven-drying alkyd system in previous study. In addition, the final thermal oxidative degradation temperatures of ALK-UA and ALK-CHF blends were higher than those of alkyd-amino resins and similar alkyd-ketone combinations (500–650 °C) given in the literature [39–41, 48, 119]. Moreover, the residual content of heat stable/thermal resistant ALK-CHF blends with 20 and 50% CHF resin was high and it was around 10–20% at 800 °C. So, they may be preferred for intumescent and fire retardant coating applications. In addition, the blends prepared in this study reached the dry-to-touch stage quickly (in about 30 minutes, especially the CHF resin systems) and reached the through-dry stage in 24 h in air-drying. Considering the good physical, excellent chemical, and further improvable heat-stable properties of these films as well as thorough drying time that can be shortened by curing at 130 °C for 1 h, it is predicted that they may be suitable for both air-drying and oven-cured systems. As a result, these promising ALK-UA and ALK-CHF blends (with or without PET) can be preferred for alternative air-drying systems that can compete with the properties of oven-cured amino resin combinations prepared with short-oil alkyd resins. Moreover, it should be noted that blends containing PET will provide

Table 16. The comparative table of physical coating properties for the alkyd-aldehyde and alkyd-ketone combinations in the literature.

Reference	Product	Drying conditions	Drying property	Hardness	Gloss at 60°	Impact resistance Abrasion resistance	Adhesion strength
Alkyd-ketone combinations							
[47]	Ketone-aldehyde pigment paste in the alkyd resin paint[a]	Thick, viscous, resinous color material	Good rheological properties	For hard resins	89–92% good clarity	–	–
[48]	Palm stearin oil-castor oil-alkyd/CHF Palm stearin oil-linseed oil-alkyd/CHF	Air-drying (1 week for tests)	55 min 55 min set-to touch	20 König s 20 König s	79% 81%	*I:* 125 kg·cm 130 kg·cm	100% 100%
[49]	Alkyd/castor oil-epoxy resin condensate/CHF	Air-drying (168 h for tests)	40 min surface dry	Pencil hardness: 4H	–	*I:* 175 lb·in (86.4 kg·cm)	Pass
[50]	Linseed oil-pentaerythritol alkyd/CHF	Air-drying (1 week for tests)	40 min surface dry	Pencil hardness: 5H	83%	–	100%
[51]	Linseed oil-glycerin alkyd/CHF	Air-drying (1 week for tests)	50 min surface dry	Pencil hardness: B	80%	*I:* 100 lb·in (115.2 kg·cm)	82%
This study	ALK-CHF blends with different ratios (Reference and PET alkyds with TOFA)	72 h air- drying + 1 h at 130 °C	45–60 min 30–60 min dry-to touch	97–140 93–106	139–140 90–105 GU	*I:* >200 kg·cm *A:* 500–1400 900–1450 mL sand	100%
Alkyd-aldehyde combinations							
[45]	Modified urea-aldehyde products (*in situ* urea-aldehyde alkyd product)[a]	Heat-hardening	–	Full heat hardening type hardness	Goss for varnish coating	Plasticizer for nitro cellulose (NC) resins	Adhesive for NC resins
[46]	Paint formulation (urea-aldehyde resin + long-oil alkyd resins)[a]	Suitable for brushing, spraying or casting	–	Good mechanical properties	Good gloss	Appropriate for plasticizer combinations	For metal, wood, chip board and paper substrates
This study	ALK-UA blends with different ratios (Reference and PET alkyds with TOFA)	72 h air-drying + 1 h at 130 °C	180 min 120 min dry-to touch	80–135 73–112 König s	144–148 91–98 GU	*I:* >200 kg·cm *A:* 450–650 800–1300 mL sand	100%

[a] There are no test results for the coating properties that are directly comparable.
Abbreviations: *A:* abrasion,
I: impact

environmentally friendly and profitable applications beside a positive contribution to coating properties.

4. Future perspectives

Current status and future expectations

Alkyd resins have many superior properties, as mentioned above and are used in many areas depending on their existing superior properties. However, some of their weak properties may need to be improved depending on the use area. In some cases, their good properties may even need to be further enhanced due to their intended use. In this direction, alkyd resins have been modified with many resins in different ways. Nevertheless, there are only a few studies that have focused on using aldehyde or ketone resins in alkyd modifications. The combination of these resins with alkyd resins has not been extensively studied. Although there are few studies on this type of coating combination containing urea-aldehyde or cyclohexanone formaldehyde and alkyd resins, there are several patent studies that explore the use of different types of aldehydes or ketones with alkyd resins or a combination of different aldehydes/ketones with alkyd and other resins. The literature contains various patent studies on coatings, paint formulations, pigment pastes, *etc.,* which are made using different aldehyde and ketone structures. Currently, the low molecular weight UA and CHF resins used in this study have a wide range of applications due to their solubility, compatibility with many resins, and

Table 17. The comparative table of chemical coating properties for the alkyd-aldehyde and alkyd-ketone combinations in the literature.

Referene	Product	Alkali resistance	Acid resistance	Water resistance	Salt resistance	Solvent resistance	Environmental resistance
Alkyd-ketone combinations							
[47]	Ketone-aldehyde pigment paste in the alkyd resin paint[a]	–	–	Good pigment wetting	–	Wide solubility	Wide compatibility with resins
[48]	Palm stearin oil-castor oil-alkyd/CHF Palm stearin oil-linseed oil-alkyd/CHF	U-24 h U-24 h 0.5 N KOH	CU-24 h CU-24 h 10% HCl	PA-24 h U-24 h water	CU-24 h CU-24 h 10% NaCl	–	–
[49]	Alkyd/castor oil-epoxy resin condensate/CHF	LA-2 h 3% NaOH	SLG-24 h 5% HCl	LG-168 h water	–	SLG-168 h xylene	–
[50]	Linseed oil-pentaerythritol alkyd/CHF	–	U-24 h 3% H_2SO_4	B-24 h water	–	–	NS 4 months (skinning endency)
[51]	Linseed oil-glycerin alkyd/CHF	–	U-24 h 3% H_2SO_4	BR-HB 24 h water	–	–	NS 4 months (storage stability)
This study	ALK-CHF blends with different ratios (Reference and PET alkyds with TOFA)	NA 24–72 h 3% NaOH (PET-based)	NA-72 h 3% H_2SO_4	NA-18 h water	NA-72 h 5% NaCl	NA-30 min T-M-EA	NA 10 cycle (wet-dry-cold-heat)
Alkyd-aldehyde combinations							
[45]	Modified urea-aldehyde products (*in situ* urea-aldehyde alkyd product)[a]	Retain alkali resistance characteristic of urea-aldehyde resins	–	–	–	Soluble in common commercial solvents	Suitable for use in adhesives, plastics and coatings
[46]	Paint formulation (urea-aldehyde resin + long-oil alkyd resins)[a]	–	—	Good water resistance	–	Unlimited solubility in aliphatic hydrocarbons	Good resistance to heat yellowing, outstanding lightfastness
This study	ALK-UA blends with different ratios (Reference and PET alkyds with TOFA)	NA 24–48 h 3% NaOH (PET-based)	NA-72 h 3% H_2SO_4	NA-18 h water	NA-72 h 5% NaCl	NA-30 min T-M-EA	NA 10 cycle (wet-dry-cold-heat)

[a] There are no test results for the coating properties that are directly comparable.

Abbreviations: B: blush,
BR-HB: brittle and heavily blushed,
CU: completely unaffected,
LA: largely unaffected,
LG: loss in gloss,
NA: not affected,
NS: no skinning,
PA: partially affected, res: resistance,
SLG: slight loss in gloss,
T-M-EA: toluene, methanol, ethyl acetate,
U: unaffected.

excellent pigment-wetting properties. They are generally used as additives in paints, printing inks, and other coatings, especially in pigment pastes. Depending on the system they are applied, they improve properties such as gloss, drying, hardness, adhesion, UV, yellowing, water and heat resistance, resistance to weather conditions, and pigment-wetting. Today, the application area of these aldehyde and ketone resins is wide, open to research, and still attractive. This study aims to further improve the properties of alkyds by using UA and CHF resins, which have positive contributions to many coating properties and cross-linked network formation, together with alkyd resins. In addition, coating materials were obtained from alkyd-aldehyde and alkyd ketone blend with also the contribution of waste PET product. Thus, new alkyd-aldehyde and alkyd-ketone combinations with or without PET can be developed as alternative air-drying systems to compete with the properties of oven-curing alkyd amino resin combinations, such as short-oil alkyd-melamine formaldehyde and alkyd-urea formaldehyde. The films of these coating materials reached to the dry-to-touch stage within 30 min, and 6th drying degree (corresponding to the through-dry stage) at the end of the 24 h in the air. In further studies, it may be possible to reach the 7th drying degree (full-dry) in the air in a shorter time by trying different formulations for the blends with waste PET. Additionally, it may offer faster drying by changing the oil ratio, oil type and composition of the oil mixture in the alkyd synthesis for the blends without waste PET. It would be beneficial to change the UA and CHF resin ratios used in blends and to try different ratios of the resin combinations depending on the desired properties to be improved. In addition, it is also possible to obtain raw depolymerization products or purified depolymerization intermediates with different functionalities through depolymerization reactions performed under different reaction conditions and to use these recycled products in the alkyd resins synthesis with different properties. At present, there are many studies on PET depolymerization in the literature. The product properties obtained by the depolymerization reactions and alkyd resin composition can be changed according to expectations. Depending on the process conditions, the field of use, and expectations from the final product, it is possible to carry out different reactions such as hydrolysis, glycolysis, aminolysis, and their simultaneous applications for depolymerization. Thus, it can yield depolymerization products with different compositions and functionalities and allow for the design and production of various alkyd resin formulations. It notes that the optimum ratios will also change depending on the conditions and expectations of each process. In this context, it is predicted that the reference and PET-based alkyd-aldehyde and alkyd-ketone blends prepared through this study and other possible formulations that can be prepared will take place in the coating sector as an alternative, sustainable, and valuable product.

5. Conclusions

In this study, we prepared waste PET-based alkyd-aldehyde and alkyd-ketone blends that can be used in coatings for versatile applications with a green technology approach for the first time. To further enhance the superior coating properties of alkyd resin and improve the weak points, we used both aldehyde (UA) and ketone (CHF) resins to contribute to cross-linked network formation. Thus, we used low molecular weight aldehyde and ketone resins, which are generally used as additives in the coating industry, as the main components in coating materials and successfully integrated them into the structure. Further, we also prepared reference counterpart combinations without PET alongside PET-based alkyd-aldehyde and alkyd-ketone combinations with waste PET depolymerization products (DP). For this aim, we conducted a four-stage study to modify waste PET-based alkyd resins using aldehyde and ketone resins. First, we carried out simultaneous hydrolysis-glycolysis of waste PET at high pressure to obtain waste PET depolymerization product having both hydroxyl and carboxyl end-groups, which can react easily with other components contained in the formulation of the alkyd resin. In the second stage, we synthesized tall oil fatty acid (TOFA) based long-oil alkyd resin containing waste PET depolymerization product to evaluate recycled PET. Next, we modified the synthesized reference (without PET) and PET-based alkyd resins with aldehyde and ketone resins, which can support and assist the formation of the cross-linked network by additional cross-linking reactions in various ratios for preparing alkyd-aldehyde and alkyd-ketone blends. Finally, we conducted coating tests and thermal analyses of prepared blends and compared the results with blends prepared with reference alkyds that do not contain waste PET. In summary, in this comprehensive study, alkyd-aldehyde (ALK-UA) and alkyd-ketone (ALK-CHF) blends with and without PET were prepared for the first time. Structural analysis, physical and chemical coating properties, and thermal behaviors were investigated comparatively. Our results are summarized below:

Long-oil reference (without PET) and PET-based alkyds (AREFT and APETT) showed good compatibility with both urea-aldehyde (UA), and ketone (CHF) resins, and completely homogeneous reference and PET-based cross-linked compact blend films were prepared successfully. During air-drying and then oven-curing of ALK-UA and ALK-CHF blend films, cross-linking reactions probably caused by free hydroxyl, carboxyl, and methylene groups in the alkyd, and carbonyl groups in the ketone, and hydroxyl groups in the aldehyde were simultaneously effective. In general, in both the ALK-UA and ALK-CHF blend series, the modification with both UA resin and CHF resin was improved to the physical and chemical coating properties of individual alkyd resin. CHF resin was also improved to the thermal stability of alkyd resins.

The addition of UA or CHF resin as a modifier to alkyd resin generally shortened the dry-to-touch time in both blend series. Among all blends, the shortest touch dry time of 30 min was obtained in PET-based ALK-CHF blend films containing 40 and 50% CHF resin ratios.

The ALK-UA blend series prepared using reference and PET-based alkyd resins with UA resin provided medium-hard/hard and gloss/high gloss films with excellent adhesion and impact resistance. These films also demonstrated superior resistance to acid, salt, water, and environmental factors. In both reference and PET-based blends, as the amount of UA resin increased, the hardness and alkali resistance of the films increased. Notably, the PET-based ALK-UA blends exhibited higher alkali resistance than their reference counterpart blends. In the ALK-CHF blend series prepared with reference and PET-based alkyd resins and CHF resin, the medium hard/hard, and gloss/high gloss films having excellent adhesion and impact resistance were obtained. These films had resistance to acid, salt, water, and environmental factors, as well as high heat stability/thermal resistance. The blend with 50–50% PET-based alkyd-CHF resin showed excellent solvent resistance.

The blends with CHF resin had better alkali resistance than those with UA resin. In PET-based ALK-CHF blends, alkali and thermal resistance significantly increased with the incorporation of the CHF resin into the alkyd resin. Moreover, in both reference and PET-based ALK-CHF blends, the increase in the CHF resin ratio led to faster drying, increased hardness, improved alkali resistance, and enhanced thermal resistance. In addition, PET-based ALK-CHF blends containing a ratio of 20 and 50% CHF resin had high residual contents of ~10 and ~20% at 800 °C. The use of waste PET depolymerization products did not show a negative effect on the physical/chemical coating and thermal properties of alkyd resin and blend films. On the contrary, mostly much better (in some cases superior) results were obtained than individual alkyd resin. It means that the properties of alkyds have been further improved by using depolymerization products as well as modifier resins. These contribute to various coating properties and have the potential to provide additional support for cross-linked network formation. Especially in blends prepared with PET-based alkyd resin and CHF resin, the use of CHF at ratios of 30% and above offered the best results in almost all properties. These PET-based ALK-CHF blend films, which reached the completely dry stage after 24 h, could be used in air-drying systems with the appropriate formulation improvements. Alternatively, they may also be possible to use in baking or stoving systems by shortening the drying times through oven-curing. Considering the good physical, excellent chemical, and further improved heat-resistant properties of these films, they can be preferred as alternative air-drying systems that can compete with the properties of short-oil oven-cured alkyd-amino resin combinations. Additionally, another probability is that ALK-CHF blends with a higher residual content may be included in intumescent coating formulations, potentially supporting the formation of a larger residual char layer and possibly increasing flame retardancy.

As a result, at the end of this study, improved/advanced alkyd blends having superior properties were developed by incorporating waste PET recycling products into the alkyd resin structure as raw materials and modifying these alkyds with aldehyde and ketone resins. These blends are expected to be considered as a high value-added, sustainable, and environmentally friendly alternative for designing versatile coatings for various applications.

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