Research Highlight

A Novel Approach to Synthesis Alkyd Resin from Recycled Polyethylene Terephthalate (rPET)

Bhagyesh Sunil Chavan * and Vrijeshkumar Singh

Asian Paints Research and Technology Centre, Turbhe, Navi Mumbai 400703, India; vrijeshkumar.singh@asianpaints.com (V.S.)

* Corresponding author. E-mail: bhagyesh.chavan@asianpaints.com (B.S.C.)

ABSTRACT: Reducing carbon footprints is an essential requirement in the chemical industry. Researchers are concentrating on creating sustainable products derived from renewable resources or waste materials. Polyethylene terephthalate (PET) waste significantly contributes to carbon footprints; the chemical recycling of PET waste possesses extensive opportunities within the chemical sector. For instance, PET waste can be transformed into valuable alkyd resin, which is utilized in the production of oil-based paints. This research work focuses on the synthesis of long oil alkyd resin using recycled polyethylene terephthalate (rPET). As the incorporation of rPET in alkyd resin has several limitations such as two-step synthesis, inability to produce long oil alkyd, and long drying time. To overcome these limitations, a novel synthesis route has been devised to produce long oil alkyd resin. In this study, three long oil alkyd resins were synthesized, each containing varying amounts of rPET. The presence of rPET in the alkyd resins was confirmed by spectroscopic techniques. To assess the impact of rPET content on alkyd resin, physicochemical properties, performance testing, and instrumental analysis have been conducted. A comparison is made between these resins and the benchmark long oil alkyd resin, and the results are discussed. Furthermore, to synergize the coating applications, viscoelastic behavior and mechanical properties of the dried films were assessed, including exterior durability. Alkyd resin containing 8% rPET shows performance properties that are comparable to the benchmark alkyd resin. This alkyd requires 80 min for surface drying and 4 h to reach a tack-free state. It has a gloss value of 86 at 20° angle. The scratch hardness is recorded as 900 g, while the gloss retention stands at 88.34% following 240 h of QUV exposure. This novel synthesis route helps to incorporate the rPET in the alkyd backbone with reduced carbon footprint to meet the goal of sustainability and the circular economy.

Keywords: Recycling; rPET; Long oil alkyd; Sustainability; Circular economy

1. Introduction

1.1. Significant Environmental Issue: Global Warming

Global warming is recognized as a critical challenge worldwide due to its harmful impact on the environment. A goal has been established to reduce global greenhouse gas emissions by 2.6 percent by 2030, relative to 2019 levels, as per the UN Environment Programmer's (UNEP) Emissions Gap Report

2024 [1]. This imposes a considerable obligation on every nation to tackle this issue. To meet this target, emissions must be cut by 43 percent by 2030, with the aim of achieving net zero by 2050 [2,3]. Various initiatives are being implemented across all sectors globally to minimize carbon footprints. In particular, the chemical industry is focusing on developing sustainable products to address environmental issues, including waste management and the depletion of fossil fuel resources.

1.2. Polyethylene Terephthalate (PET): Major Contributor to Plastic Waste and Environmental Issues

Plastic waste is one of the major contributors to carbon emissions, particularly polyethylene terephthalate (PET), which is widely used in commodity applications [4,5]. The global production of PET exceeds eighty-two million metric tons annually, making it a significant source of waste and environmental problems [6,7]. The waste PET is utilized across various sectors, including textiles, packaging, construction, chemicals, and coatings by chemical recycling. In the coatings industry, PET waste undergoes chemical recycling to produce alkyd and polyester resins [8].

1.3. Global Market of Alkyd Resin

Alkyd resin, a workhorse in the paint industry, offers various properties, such as flexibility, gloss, and air-drying capability, making it a popular choice for coatings [9]. The worldwide market for alkyd resins is projected to increase from USD 23 billion to approximately USD 39 billion by the year 2030, reflecting a compound annual growth rate of about 7.5% [10,11]. Basically, alkyd is an oil-modified polyester resin produced through the condensation reaction of polyols with polybasic acids to form ester linkages [12]. rPET has been used in the production of as such polyester resin at commercial scale, but producing alkyd (oil-based polyester) faces a number of challenges [13,14]. As triglyceride (oil) is integrated into polyester reactions through monoglyceride formation via the transesterification reaction with polyol. Alkyd is categorized based on the percentage of oil content in an alkyd, like long oil alkyd (oil content exceeding 55%) utilized in air drying systems for decorative enamels, industrial enamels, and wood finishes. Medium oil alkyd (45–55% oil length) is employed in primer applications for decorative and industrial coatings. Short oil alkyd (less than 45% oil length) is suitable for quick-drying industrial paints, auto-refinish, wood coatings, and more [15]. The oil length formula is given in Equation (1) below. The best way of chemical recycling of rPET is the utilization of rPET into alkyd resin synthesis.

$$\text{Oil Length} = \frac{\text{Oil percent in Alkyd}}{100 - (\text{Water of Reaction} + \text{Solvent Mass})} \times 100 \tag{1}$$

1.4. Utilization of Recycled Polyethylene Terephthalate in Alkyd Resin Synthesis

The conventional method for chemical recycling of PET involves glycolysis, in which ethylene glycol breaks the ester linkage to form bis(2-hydroxylethyl terephthalate) (BHET) [16]. This BHET is then used in the alkyd esterification reaction, as demonstrated by Nawal E. et al., who synthesized the medium oil alkyd resin from glycolyzed PET waste using propylene glycol and diethylene glycol [17–19]. Vandana Jamdar et al. also explored chemical recycling of PET waste through reaction with ethylene glycol [20]. Büyükyonga et al. investigated the glycolysis reactions of waste PET flakes using dipropylene glycol, diethylene glycol, and triethylene glycol, with the resultant products used in the formulation of medium-oil acrylic-modified water-reducible alkyd resins [21]. Spasojević et al. investigated the glycolysis of waste PET using multifunctional alcohols such as glycerol, trimethylolethane, trimethylolpropane, pentaerythritol, diethylene glycol, propylene glycol, and dipropylene glycol, which were then utilized in alkyd resin synthesis [22]. While the conventional approach has several limitations like two-step synthesis, inability to produce long oil alkyd, and long drying time. The new proposed synthesis route presented in this research work offers the advantage of a single step synthesis methodology that directly introduces rPET into the

reactor during alkyd resin synthesis, allowing for simultaneous rPET depolymerization and resin formation, partially replacing the petroleum-based polyol or polyacid typically used in the resin composition. This innovative approach provides satisfactory drying time and improved performance properties. The main objective of this research work is to produce a sustainable product that aligns with the principles of the circular economy, aiming to replace the end-of-life of PET waste with a model focused on sharing, leasing, reusing, repairing, refurbishing, and recycling polyethylene terephthalate as long as possible [23].

This research focused on the creation of three long oil alkyd resins utilizing rPET, soybean oil, glycerin, pentaerythritol, phthalic anhydride, dibutyl tin-oxide (DBTO) as a catalyst and ortho xylene as azeotropic solvent. Incorporating different proportions of rPET, Alkyd A includes 8% rPET, Alkyd B has 12% rPET, and Alkyd C comprises 16% rPET. The performance of these resins was evaluated against the benchmark Alkyd D, which does not contain rPET.

2. Experimental

2.1. Materials

Alkali refined soybean oil industrial grade sourced from Adani Wilmer Pvt Ltd. (now often operating as AWL Agri Business Ltd., Ahmedabad, India). The recycled polyethylene terephthalate (rPET) material is acquired from Dalmia Polypro Industries Pvt Ltd., Mumbai, India, with its properties provided in Table 1. Dibutyl tin-oxide (DBTO) catalysts of 98% assay are obtained from Guldbrandsen Chemicals Private Ltd., Vadodara, India. Refined Grade Glycerin with Glycerol content of 98% supplied by Godrej Industries, Mumbai, India. While Phthalic Anhydride of 98% purity is purchased from Thirumalai Chemicals Limited, Chennai, India. Pentaerythritol of Penta Mono grade obtained from Perstorp Chemicals, Mumbai, India. Ortho xylene of 98% purity is utilized from Reliance Industries, Mumbai, India. Mineral turpentine oil (MTO) is obtained from Bharat Petroleum Corporation Limited, Mumbai, India. Cobalt octoate, with a 5% metal content, is used as a surface drier from Arum Pharmachem Pvt. Ltd., Mumbai, India. Zirconium octoate, containing 18% metal content, is employed as a through drier from Notional Specialties Products Company, Vapi, India. Calcium Octoate, with a 3% metal content, is utilized as an auxiliary drier from Bhagwati Allied Products, Chhatrapati Sambhajinagar, India.

Table 1. Properties of recycled PET used for the experimentation. (As per supplier COA).

Sr. No.	Tests	Units	Results
1	Visual Appearance	-	Flakes
2	Intrinsic Viscosity	dL/g	0.698
3	Moisture	Percentage	0.47
4	Ash	Percentage	0.29
5	Bulk Density	Kg/m^3	310
6	Flakes Dimension	mm	8 to 13 (70%) 2 to 8 (30%)
7	Water pH before and after washing flakes	-	7.5

2.2. Methods

2.2.1. Synthesis of Alkyd Resin Based on rPET

Alkyd A (8% rPET), Alkyd B (12% rPET), and Alkyd C (16% rPET) were synthesized based on the formula of Alkyd D as detailed in Table 2. This formula includes zero percentage of rPET. As we increase the amount of rPET in the formula, the raw materials such as soybean oil, glycerin, DBTO, and ortho xylene remain constant. However, as the quantity of rPET increases, the amounts of raw materials like pentaerythritol and phthalic anhydride decrease in proportion to the quantity of rPET. The synthesis of

alkyd resin was conducted in 2-L 4 neck round bottom flask equipped with a stirrer, dean & stark, temperature sensor, water condenser and nitrogen purging tube. The flask was placed in a heating mantle to ensure uniform heating [24]. The stirring speed is maintained at 180 ± 10 rpm. The soybean oil, glycerin, pentaerythritol, and DBTO catalyst were added at room temperature. The heating rate was adjusted to reach the final temperature of 245–250 °C. After one hour of reaching the 245 °C temperature, a sample was taken to measure the extent of monoglyceride formation using alcohol tolerance [25]. Once the desired alcohol tolerance was achieved, the heating of the reaction was stopped. At a temperature of 190 °C, recycled PET flakes were added and heated up to 240 °C for 1 h. Within this hour, the recycled PET underwent depolymerization, resulting in a clear material in the system. The reaction scheme is shown in section 3.2. After 1 h, the material was cooled to 170 °C, and phthalic anhydride, along with ortho-xylene (azeotropic solvent), was charged [26]. The heating was then restarted, and the reaction temperature was raised to 230 °C. Acid value and viscosity of the batch were monitored after the removal of 80% water of the reaction based on the theoretical value [27]. Once the desired acid value and viscosity were achieved, the azeotropic solvent ortho-xylene was removed from the system by flushing with nitrogen gas. The batch was thinned to 60% solids at 170 °C using mineral turpentine oil.

Table 2. Formulation of Alkyd Resin.

Raw Materials	Parts by Weight	Molecular Weight (g/mol)
Soyabean oil	55.0	880
Pentaerythritol	7.0	136
Glycerin	8.0	92
DBTO	0.05	248
rPET	0	Not applicable
Phthalic Anhydride	26.80	148
Ortho Xylene	3.15	106
Total	100	

2.2.2. Characterization

Physicochemical properties of the alkyd resins, such as acid value (ASTM D1639), viscosity (ASTM D1545), colour (ASTM D1544), non-volatile matter, and drying, were studied. Differential Scanning Calorimetry (DSC) analysis is used to determine the percentage crystallinity of the rPET sample. The DSC instrument used was TA Instrument Discovery DSC250 Auto by TA Waters, New Castle, DE, USA. The instrument conditions are equilibrate at 0 °C, 0 to 300 °C @ 10 °C/min. The FTIR spectroscopy was utilized to detect the presence of rPET in the alkyd resin. The FTIR analysis was conducted over a range of 4000–400 cm^{-1} with 16 scans on the FTIR-ATR device model Frontier by PerkinElmer India Private Limited, Thane city, India. The molecular weight of the alkyd resins was determined through Gel Permeation Chromatography, using the Agilent 1260 multi detector system by Agilent Technologies, Santa Clara, CA, USA. Dynamic mechanical analysis (DMA) was performed using the DMAQ 800 equipment by TA Waters, New Castle, DE, USA. With a temperature sweep test ranging from −30 to 150 °C at a rate of 3 °C/min, strain of 0.1%, and frequency of 1 Hz. Stress was applied to the system, and the resulting strain was measured. Thermogravimetric analysis (TGA) was carried out using the Mettler Toledo device TGA1 Star System by Mettler Toledo, Greifensee, Switzerland. In the temperature range of 30–600 °C at a ramp rate of 10 °C per minute under a nitrogen atmosphere with a N_2 purging rate of 50 mL/min.

2.2.3. Film Preparation and Performance Evaluation Test Methods

Resin sample (100 g) was combined with 14 g of mineral turpentine oil (MTO) and driers, including 5% cobalt octoate (0.6 g), 18% zirconium octoate (1.67 g), and 3% calcium octoate (4 g) [28]. The quantity

of driers used depended on the solid content of the binder. A uniform solution was prepared by stirring and mixing, it was left to sit overnight before being applied to metal panels. Dry film thickness was measured in accordance with ASTM D5796 using a Positector 6000 thickness gauge, while gloss was measured following ASTM D523 with a gloss meter. Scratch hardness was determined using an automatic scratch hardness tester REF 705, as per ASTM D5178. Pencil hardness was evaluated according to ASTM D3363, with hardness expressed as H, 2H, 3H, or 6H. The crosscut adhesion test was conducted following the ASTM D3359 standard. Image clarity was assessed based on the distinctness of the image (DOI) according to ASTM D5767. Impact resistance was tested using an Erichsen impact testing machine, as per ASTM D2794. The flexibility test was conducted using a conical mandrel tester in accordance with ASTM D4145. Weathering effect was studied by QUV (ASTM G53-96) by Q Lab solar eye, Westlake, OH, USA. The testing condition was an alternate cycle of 4 h UV and 4 h condensation. UV temperature 49–51 °C, Condensation Temperature 44–46 °C, Irradiance level 0.54–0.056 watts/m^2/nm.

3. Results & Discussion

3.1. DSC Analysis of rPET

The depolymerization process of rPET is significantly influenced by its crystallinity. The crystalline regions are denser, more ordered, and chemically resistant, making ester bonds less accessible to depolymerization. This necessitates greater energy, time, and catalysts to break the ester bonds and achieve depolymerization. In contrast, the amorphous regions decompose at a much faster rate [29]. The percentage of crystallinity in the sample is assessed through DSC analysis. According to the literature, the enthalpy of 100% crystalline PET is 140 (J/g) [30]. The enthalpy of the rPET sample, as determined by DSC, is 41.7 (J/g), as given in Figure 1. Based on the formula, the percentage crystallinity of the rPET sample is calculated to be 29.78%. The results indicate that the rPET exhibits moderate crystallinity. This suggests that depolymerization is feasible and more efficient compared to 100% crystalline rPET. The depolymerization process is carried out at 240 °C in the presence of a tin-based catalyst, which can effectively depolymerize the rPET under these conditions.
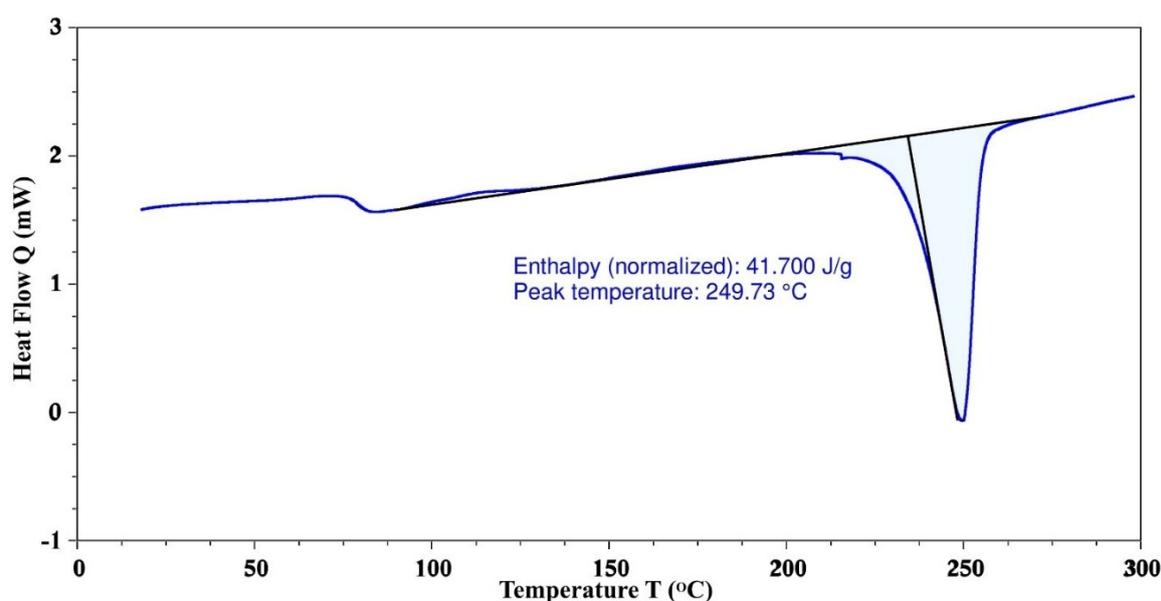

Figure 1. DSC analysis of rPET sample.

3.2. Single Step rPET Based Alkyd Resin Synthesis and FTIR Spectroscopy

The alkyd resin derived from rPET was synthesized through a single-step process. As illustrated in Figure 2a, soybean oil underwent alcoholysis with polyols such as pentaerythritol and glycerin, facilitated by DBTO acting as a Lewis acid catalyst at a temperature of 245 °C [31]. The alcohol tolerance confirms the formation of monoglycerides. All reaction samples exhibited a minimum alcohol tolerance of 1:4, indicating that monoglyceride formation has indeed occurred [32]. The FTIR spectra of the reaction products, as shown in Figure 3 confirms the formation of monoglyceride and diglyceride due to the observation of a strong –OH peak around 3464 cm^{-1}, which signifies the presence of free hydroxyl groups in the sample [33]. The carbonyl stretching at 1741 cm^{-1} further confirms the formation of esters, along with a peak at 1240–1045 cm^{-1}, typical of ester linkages. The FTIR spectra of as such rPET exhibit a carbonyl stretching at 1710 cm^{-1}, which is characteristic of the ester groups found in PET. The peaks at 1581 cm^{-1} and 1504 cm^{-1} correspond to the benzene ring present in the backbone of PET [34]. Additionally, the C–O stretching bands observed in the range of 1237–1091 cm^{-1} are associated with ester linkages [34]. Notably, there is no prominent –OH peak detected around 3400 cm^{-1}, indicating that rPET contains a minimal amount of hydroxyl groups.

After completion of monoglyceride formation the rPET chips were introduced into the reaction mixture and heated for one hour at 240 °C. In this phase, DBTO, as a Lewis acid catalyst, activates the ester bonds of rPET at elevated temperatures. A nucleophilic attack occurs from the hydroxyl groups of the monoglyceride on the carbonyl carbon of the rPET ester group, as depicted in Figure 2b [35]. This results in partial cleavage of rPET chains, releasing small ethylene glycol fragments. A linkage forms between the hydroxyl group of the monoglyceride and the rPET terephthalate units, leading to the creation of hydroxyl-terminated oligomers [36]. At this point, the reaction mixture becomes completely clear, and the sample is withdrawn, showing clarity under cold conditions. This observation indicates that depolymerization of rPET has taken place. The FTIR spectra of this reaction sample show a strong band at 1732 cm^{-1}, which is sharper than that observed in pure monoglyceride, indicating the formation of new esters [37]. The –OH band near 3464 cm^{-1} is diminished compared to that of the monoglyceride, suggesting the consumption of hydroxyl groups during the reaction. Bands at 1245–1100 cm^{-1} indicate the presence of new ester bonds. Peaks confirm the presence of an aromatic structure at 1504 cm^{-1} and 1581 cm^{-1} [38]. This confirms that the rPET has integrated into the reaction backbone.
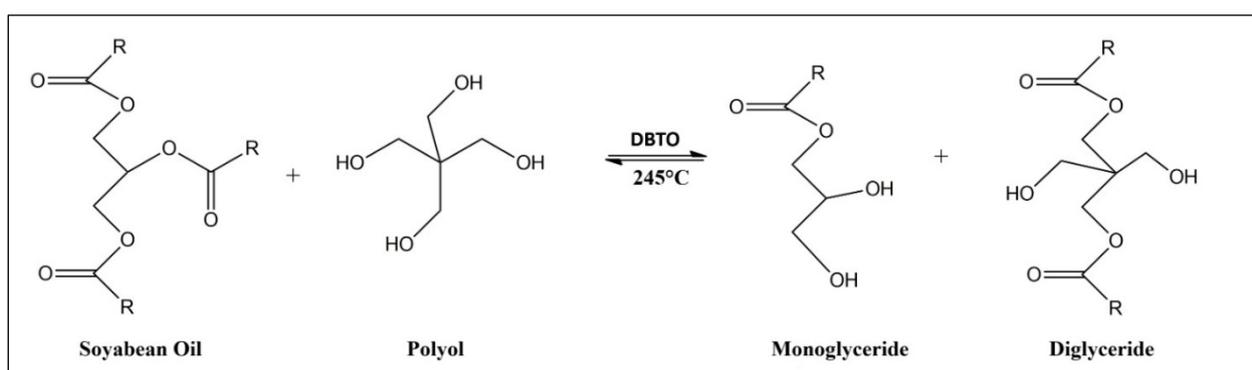
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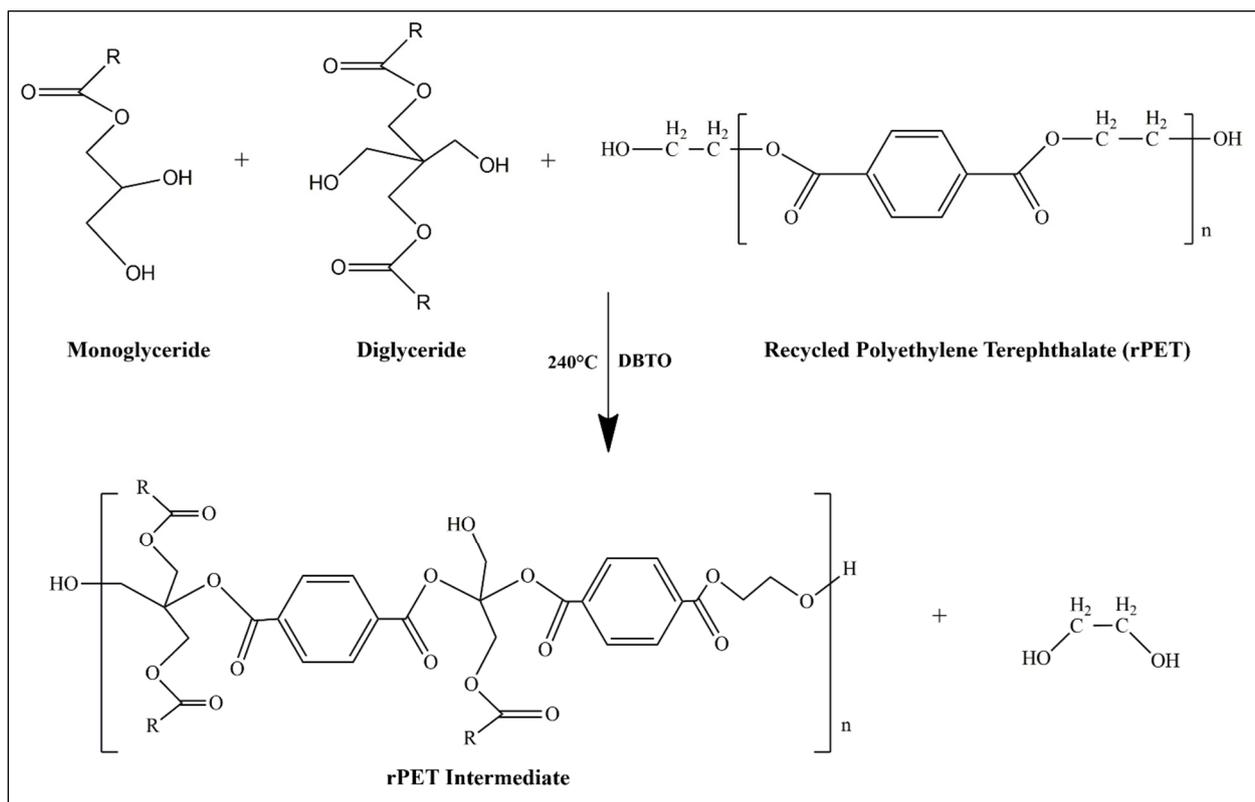
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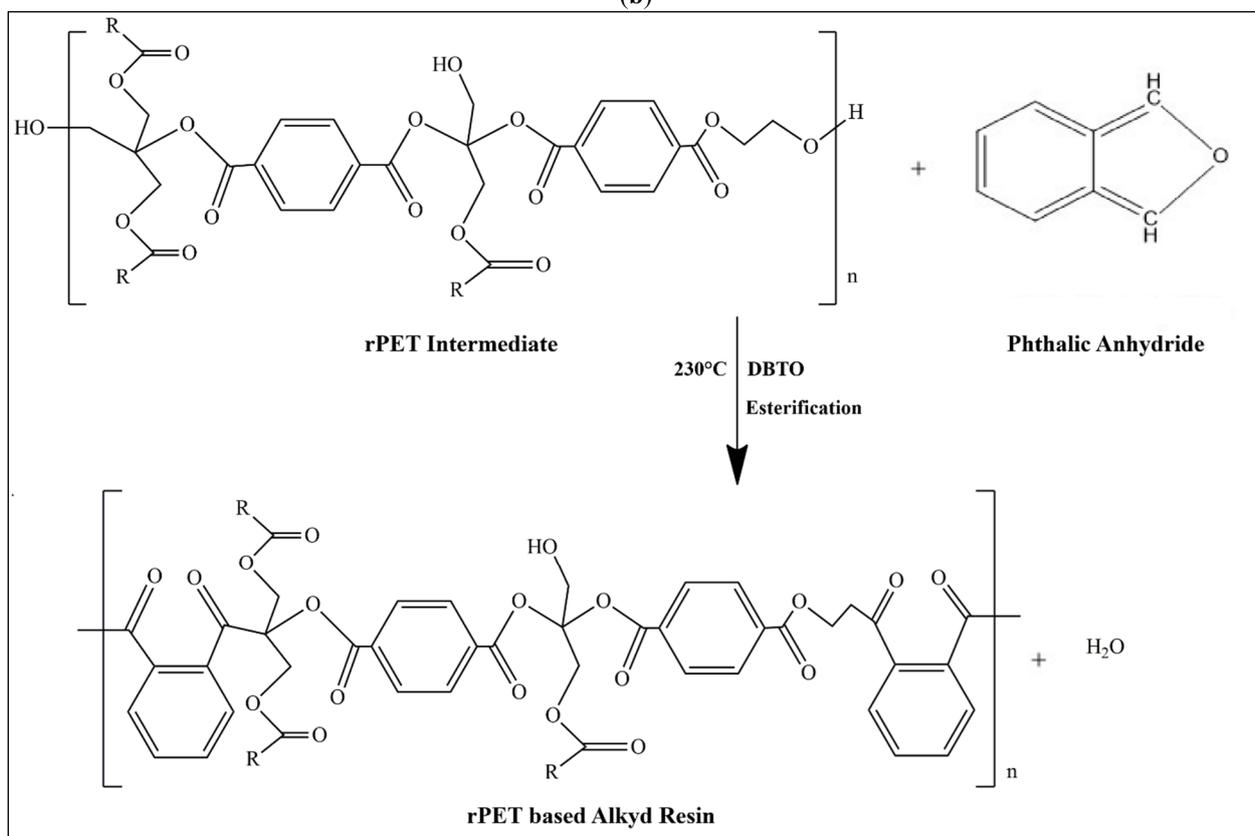
(c)

Figure 2. (a) Reaction Scheme: Synthesis of Monoglyceride; **(b)** Reaction Scheme: Synthesis of rPET intermediate; **(c)** Reaction Scheme: Synthesis of rPET based Alkyd.

After the depolymerization of rPET the reaction mass is cooled down to 170 °C. Further phthalic anhydride is added along with ortho-xylene (azeotropic solvent) and heated to 230 °C temperature for the esterification reaction. Phthalic anhydride reacts with the terminal hydroxyl of the rPET intermediate in the presence of a catalyst that will form the ester linkages, and water will be removed as a byproduct, as depicted in Figure 2c [39]. In Figure 3, if we compare the spectra of rPET based alkyd and without rPET based alkyd, the presence of a peak at 869 cm^{-1} shows the rPET integrated in the alkyd resin. This new synthesis route produced alkyd resin in one step by depolymerizing rPET in the same reactor and cooking the alkyd resin in the same reactor. Using this synthesis route long oil alkyd has been produced with shorter drying time.
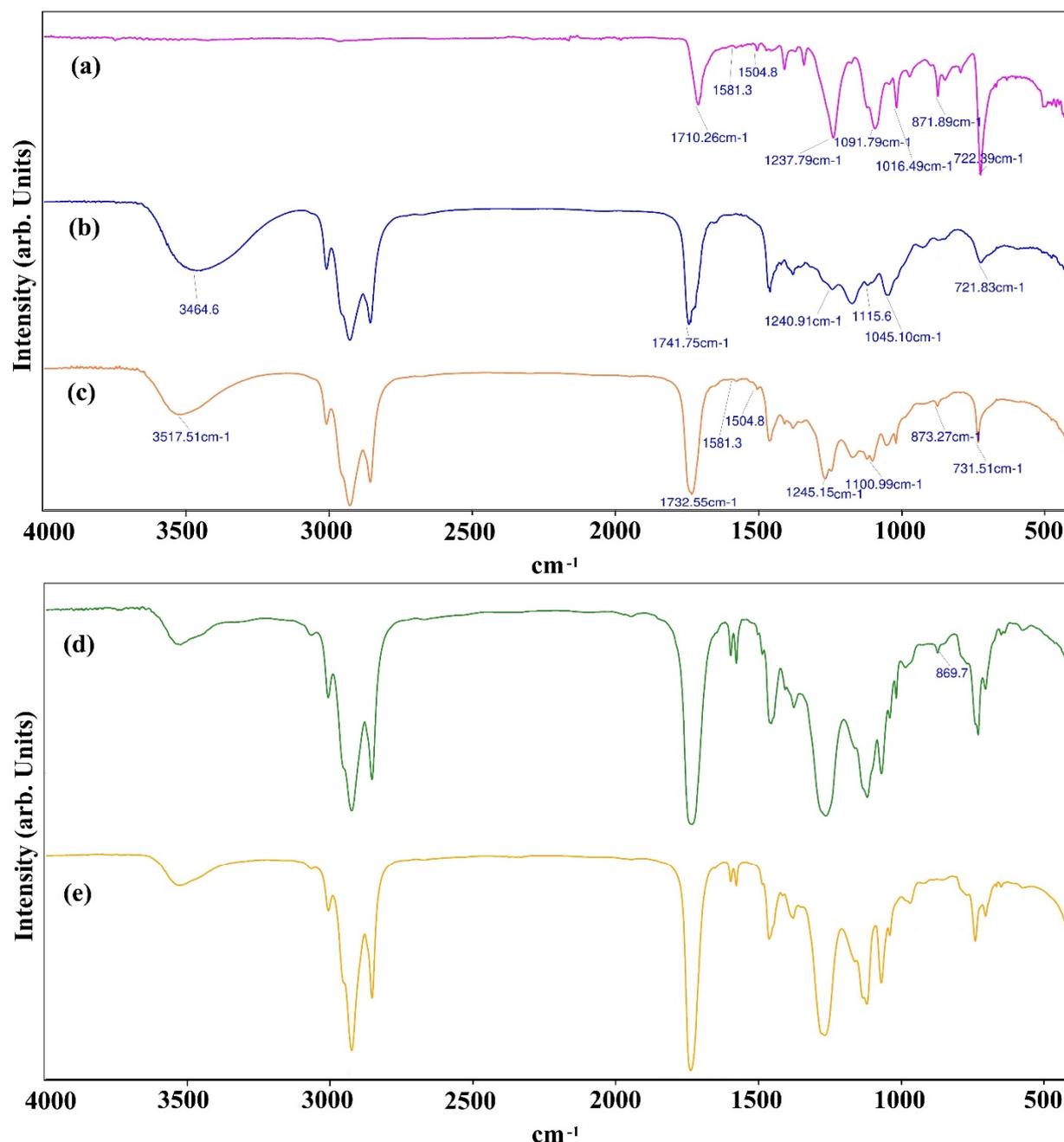

Figure 3. FTIR spectra: (a) rPET (b) Monoglyceride (c) rPET intermediate (d) rPET based Alkyd (e) Alkyd without rPET.

3.3. Physicochemical Properties

The physicochemical properties and GPC results of alkyds containing different proportions of rPET are detailed in the Table 3. All the resins underwent smooth processing and were thinned to 60% solids in MTO, resulting in completely transparent resins. The findings reveal that the color of the resins remains consistent regardless of the rPET content, falling within the 6–7 Gardner scale range. The acid value recorded was below 12 mg KOH/g. The viscosity for all resins remained consistent between W and Y on the Gardner scale at 25 °C. The drying results indicate that the alkyd resin containing 8% rPET becomes tack-free in 4.0 h, while the alkyd resin with 12% rPET achieves tack-free status in 4.30 h, and the alkyd resin with 16% rPET reaches tack-free in 8.15 h. The data suggest that as the rPET content in the alkyd increases, the drying properties are hindered. The drying process of alkyd resin is complex, occurring in two stages: the first is a physical process, and the second is a chemical process [40]. During the physical stage, the solvent evaporates, allowing the polymer chains to come together and initiate the chemical stage, which encompasses oxidation and crosslinking reactions. This chemical stage occurs in four distinct steps, oxygen induction, peroxide formation, free radical generation by peroxide decomposition, and crosslinking [41,42]. The molecular weight of the alkyd resin is critical to the drying process. The alkyd resin with 8% rPET has a reported molecular weight (Mw) of 19,727, the one with 12% rPET has an Mw of 24,197, and the alkyd resin with 16% rPET has an Mw of 31,301. The introduction of rPET in alkyd contributes to long oligomer chains by substituting smaller phthalic anhydride molecules which increase the molecular weight of alkyd [43]. The findings indicate that resins with a higher molecular weight exhibit extended drying times. This phenomenon occurs because the increase in molecular weight from rPET loading decreases the mobility of the polymer chains, thereby raising the glass transition temperature and subsequently reducing free volume. This decrease in free volume slows down the solvent diffusion rate through the film, leading to a longer tack-free time. Therefore, the alkyd containing the maximum amount of rPET has a larger molecular weight and a slower drying time, whereas the alkyd with the minimum rPET content has a lower molecular weight and a faster drying time [44,45].

Table 3. Physicochemical Properties of Alkyds.

	Alkyd A	Alkyd B	Alkyd C	Benchmark Alkyd D
Percentage of rPET (%)	8	12	16	0
Water of Reaction (%)	3.98	4.41	4.79	3.20
Alcohol tolerance achieved	1:4.0	1:Infinite	1:Infinite	1:4.5
Viscosity on Gardner scale @ 25 °C	X	W-X	X-Y	Y
Acid value (mg KOH/g)	10.1	9.25	10.92	9.02
Colour on Gardner scale	6–7	6–7	6–7	6–7
Clarity	Clear	Clear	Clear	Clear
NVM % (1 g/120 °C/1 h)	60.89	60.65	60.35	61.03
Surface Dry (minutes)	80	80	100	80
Tack Free (hours)	4.0	4.30	8.15	4.0
Hard Dry (hours)	14.0	14.0	14.0	14.0
GPC results				
Mw	19,727	24,197	31,301	26,128
Mn	2745	2683	2659	3035
Mw/Mn	7.18	9.02	11.77	8.61

3.4. Characterization of Alkyd Dried Films

The resin sample was combined with driers and thinner (MTO) as outlined in Section 2.2.3 and allowed to mature overnight. Following this maturation period, the lacquer was applied on releasing paper in

accordance with the DFT specifications. Once applied, the film was permitted to cure for 7 days before undergoing testing.

3.4.1. TGA Analysis

Using TGA, we gained insights into the thermal decomposition of the alkyd films. Table 4 illustrates the percentage weight loss, temperature, and residue at 600 °C after complete thermal decomposition, the thermogram presented in Figure 4. The findings indicated that benchmark alkyd D (without rPET) experiences weight loss at a lower temperature compared to the alkyd that contain rPET. Specifically, benchmark alkyd D exhibited 90% weight loss at 458 °C, whereas the rPET-containing alkyd showed 90% weight loss at temperatures exceeding 515 °C. This clearly demonstrates that incorporating rPET into the alkyd resin enhances its thermal stability, likely due to the introduction of long-chain and aromatic oligomers into the alkyd structure [46].
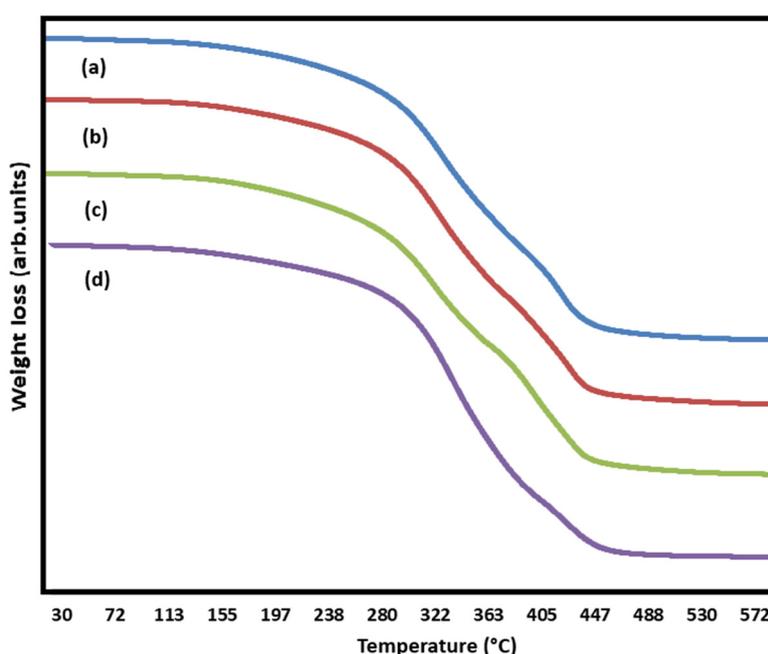

Figure 4. TGA thermogram of alkyd dried films: (a) Alkyd A, (b) Alkyd B, (c) Alkyd C, (d) Alkyd D.

Table 4. TGA results of alkyd dried films.

| Wt. Loss	Alkyd A	Alkyd B	Alkyd C	Benchmark Alkyd D
50%	369.50 °C	369.16 °C	373.00 °C	360.16 °C
60%	394.00 °C	395.00 °C	400.66 °C	376.83 °C
70%	420.16 °C	419.16 °C	419.66 °C	397.00 °C
80%	439.16 °C	440.16 °C	440.33 °C	426.50 °C
90%	553.16 °C	515.50 °C	569.50 °C	458.66 °C

3.4.2. DMA Analysis

The analysis conducted using DMA that provides insights into the viscoelastic properties exhibited by the films. These properties are closely linked to the crosslink density in the film. The crosslinked density, in turn, is influenced by factors such as molecular structure, processability, and drying characteristics of the polymer [47]. The findings are summarized in Table 5, which includes glass transition temperature and crosslinking density obtained from the DMA curve as given in Figure 5. By examining the storage modulus value in the rubbery plateau region, it is possible to determine the crosslinking density of the film, as this

value correlates with the number of crosslinks in the polymer chain [48]. The crosslinking density is calculated using the equation as given below.

$$q = \frac{E'}{3RT}$$

where, q—Crosslinking Density; E′—Storage Modulus in the rubbery plateau Region; R—Universal Gas Constant; T—Absolute Temperature.
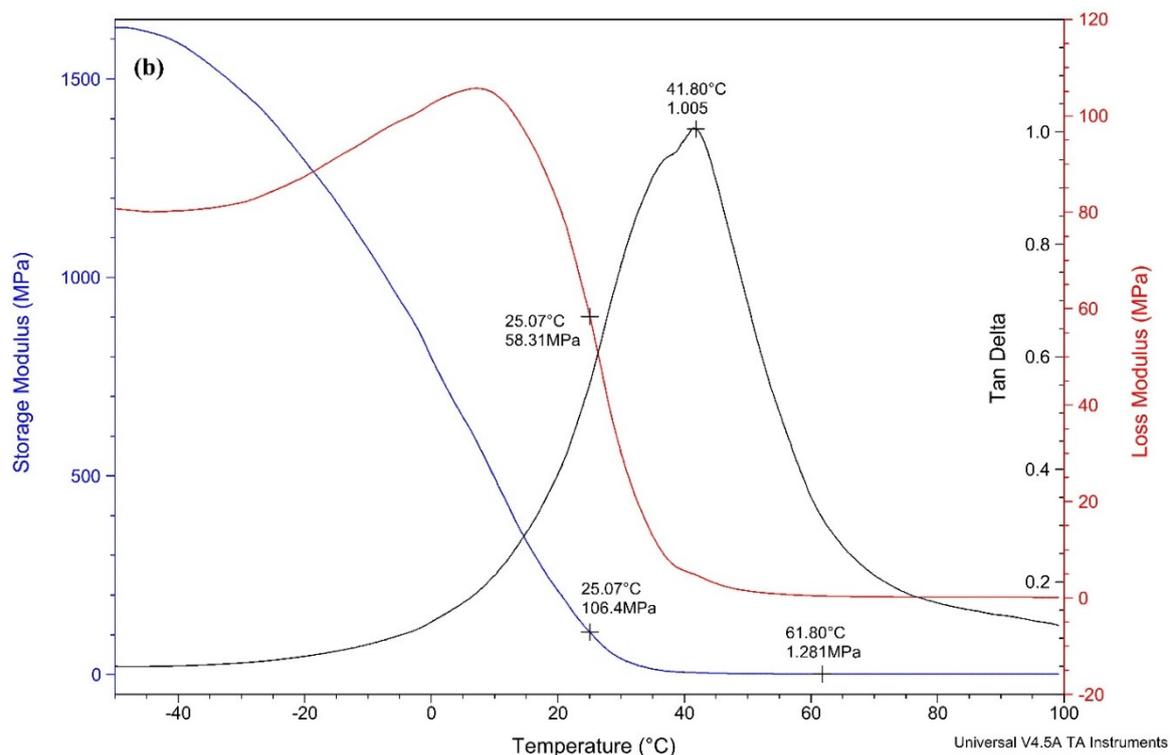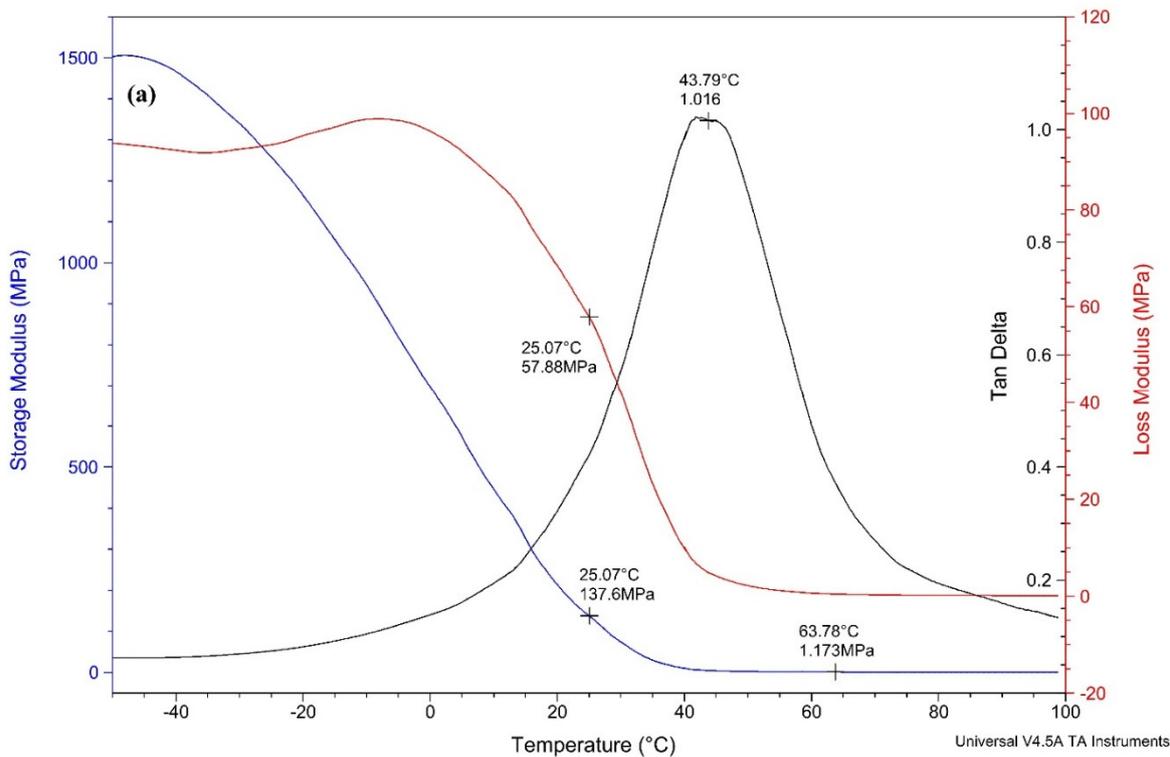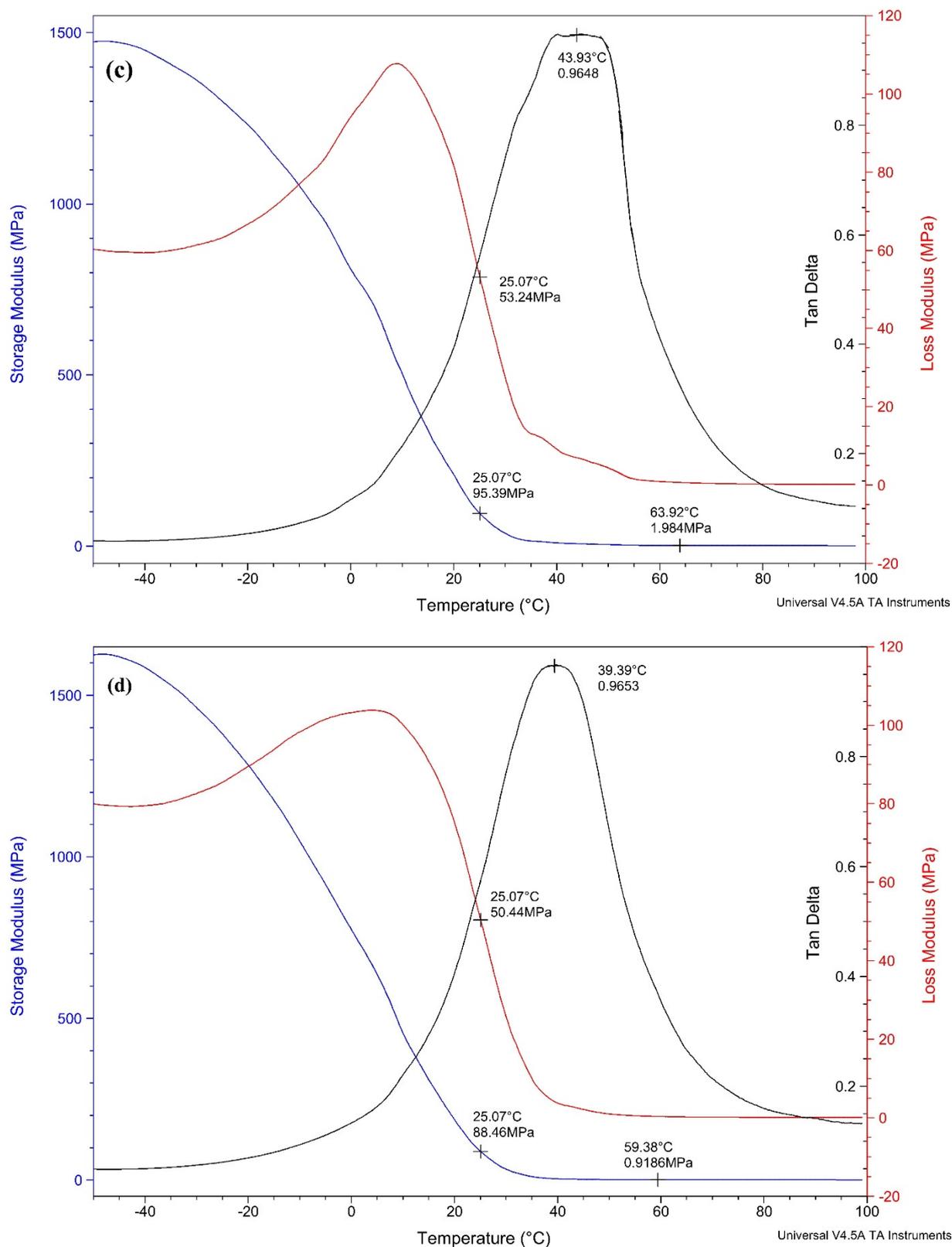
Figure 5. (**a**) DMA curve for alkyd A dried film; (**b**) DMA curve for alkyd B dried films; (**c**) DMA curve for alkyd C dried film; (**d**) DMA curve for alkyd D dried film.

Figure 5a represents the DMA curve of alkyd A loaded with 8% of rPET. The curves report a damping factor that is the tan delta value of 1.016, with the Tg value calculated is 41.7 °C

Figure 5b shows the DMA curve of alkyd B loaded with 12% of rPET. The curves show the tan delta value of 1.005, with the Tg value calculated is 43.8 °C.

Figure 5c demonstrates the DMA curve of alkyd C loaded with 16% of rPET. The curves give the tan delta value of 0.9648, with the Tg value calculated is 44 °C.

Figure 5d displays the DMA curve of alkyd D loaded with 0% of rPET. The curves result the tan delta value of 0.9653, with the Tg value calculated is 39.4 °C.

The test findings reveal that the crosslink density increases when rPET is incorporated into the alkyd resin, in contrast to alkyd resins that do not contain rPET. This suggests that long oligomer chains contributed by rPET reduce the free volume within the alkyds. As a result of this reduction in free volume, the crosslinking density is enhanced [49]. According to the observed trend, an increase in rPET content correlates with an increase in both the crosslinking density and Tg value. However, it is important to note that exceeding a certain threshold of crosslinking density may negatively affect performance characteristics.

Table 5. DMA results for alkyd dried films.

| Samples	Tg (°C)	Crosslinked Density (mol·cm^{-3})
Alkyd A	41.7	1.39×10^{-4}
Alkyd B	43.8	1.53×10^{-4}
Alkyd C	44	2.36×10^{-4}
Alkyd D	39.4	1.10×10^{-4}

4. Performance Properties of Dried Films

The transparent lacquer was prepared according to the instructions provided in Section 2.2.3 and applied to Mild Steel (MS) and tin panels, which were then left overnight to dry. The dried panels underwent various performance tests in accordance with industrial standards, and the results have been compiled in Table 6. Based on the data obtained, it can be deduced that the distinctness of the image, flow & leveling of rPET containing alkyd are comparable to benchmark alkyd. The results verified that the film exhibits uniform drying and crosslinking. The compatibility of the rPET based oligomeric reactants contributed to effective film formation, optimal flow and leveling, as well as a desirable degree of optical clarity [50]. However, the gloss tends to deteriorate as the rPET content in the binder increases. This decrease in gloss value may be attributed by the aromatic oligomers; contributed by the rPET that may increase crosslinking density caused by the excessive loading of rPET [51]. While the gloss of Alkyd A is comparable to the benchmark alkyd, the results indicate that beyond 8% of rPET loading in the alkyd, the gloss diminishes. All the samples passed the crosscut adhesion test, indicating that the resin has sufficient amounts of terminal hydroxyl and carboxyl groups that anchor to the metal substrate [52]. In terms of scratch and pencil hardness, the alkyd with the highest rPET content exhibits superior hardness properties compared to other alkyds. This can be attributed to the increased crosslinking density resulting from higher rPET loading [51]. All the samples passed impact resistance, reverse impact and flexibility test, that specify the free volume that can effectively digest the external mechanical force [53]. One of the key tests conducted in the paint industry is the QUV test. In the QUV test, the alkyd with the lowest amount of rPET demonstrated 88.34% gloss retention after 240 h, while the benchmark alkyd showed 90.29% gloss retention after the same duration as shown in Figure 6. The trend indicates that the alkyd with the highest rPET content experienced a greater loss in gloss value. This may be due to excess crosslinking of the film, which becomes brittle under QUV exposure and causes gloss to decrease [54].

Table 6. Performance tests results of alkyd clear coat.

Test	Alkyd A	Alkyd B	Alkyd C	Alkyd D
Dry Film Thickness (μm)	24–29	23–28	22–27	23–28
Distinctness of Image	Good	Good	Good	Good
Flow & leveling	Satisfactory	Satisfactory	Satisfactory	Satisfactory
Gloss@ 20° angle	86	85	79	86
Gloss@ 60° angle	103	102	100	103
Cross-cut adhesion	Pass	Pass	Pass	Pass
Scratch hardness (g)	900	900	1100	1000
Pencil hardness	H	H	2H	H
Impact resistance	Pass	Pass	Pass	Pass
Reverse impact	Pass	Pass	Pass	Pass
Flexibility	Pass	Pass	Pass	Pass
QUV weathering test (240 h)	Gloss retention 88.34%	Gloss retention 84.31%	Gloss retention 82%	Gloss retention 90.29%
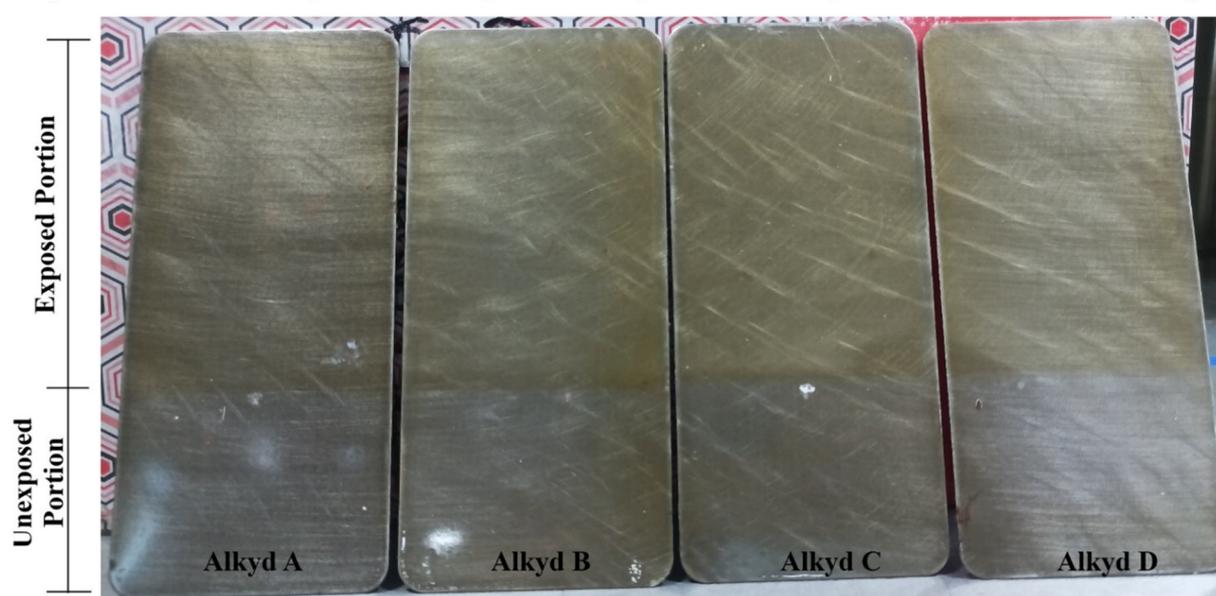
Figure 6. QUV test on Alkyd clear coat after 240 h of exposure.

5. Conclusions

The entire paint industry is exploring new approaches for sustainability. The approach of incorporating recycled polyethylene terephthalate in the alkyd resin will help in reducing the issue of PET waste and substituting the petroleum based raw material such as phthalic anhydride. Considering the production volume of alkyd resin, especially long oil alkyd, and the waste generated by PET, even a small amount of rPET incorporation into alkyd resin will have a massive impact on a larger scale.

In this research work, long oil alkyd was successfully produced by the novel synthesis route, that helped in overcoming the limitations of the conventional process of producing rPET based alkyd. Incorporating recycled PET into the alkyd resin enhances sustainability and environmental friendliness. FTIR analysis confirms the effective integration of recycled PET into the alkyd resin. GPC results reveal that increase in rPET content in the alkyd resin increases the molecular weight but affects the drying properties. This might be because of the reduction in free volume; it can be correlated with DMA results, as free volume decreases, the crosslinked density increases. The higher the rPET content in the alkyd resin higher the crosslinking density. TGA results show that the thermal stability of the alkyd film increases as the rPET content in the

alkyd increases. alkyd A, containing 8% recycled PET, exhibits comparable performance to the benchmark alkyd D in terms of drying, gloss, and hardness. In exterior durability study, alkyd with highest loading of rPET showed less gloss retention. This is mainly due to the higher aromaticity of rPET, which increases the yellowing tendency of the alkyd film, whereas alkyd A, with a lower percentage of rPET, showed comparable performance to the benchmark alkyd D. This formulation (Alkyd A) is identified as the most robust and optimized for air-drying alkyd. These findings suggest that incorporating rPET into alkyd resin using this method is a promising approach for sustainability and the circular economy principle.

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Author Contributions

B.S.C.—Conceptualization, Methodology, Formal Analysis, validation, Writing Original Draft Preparation. V.S.—Supervision, Project Administration, Resources.

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Data will be made available on request.

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The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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