Sustainable Thermoplastic Road Marking Paint Production from Natural Modified Rosins

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Modified natural rosins were evaluated as binders in the production of thermoplastic road marking paints (TRMPs). Pine rosin (GR), wood rosin (WR), and tall oil rosin (TOR) were used. Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), matrix-assisted laser desorption/ionization (MALDI-ToF-MS), and gel permeation chromatography-high pressure liquid chromatography (GPC-HPLC) were performed on natural and modified rosins. Acid number (mg KOH/g) ASTM D 465 – 05 and softening point, (°C) ASTM E 28 - 99 standard tests were applied to the samples. For the optimum synthesis condition, the pentaerythritol/rosin mol/mol ratio is 1/1, with the levels of Irganox 1425/rosin w/w, 0.5%, and TBM-6/rosin w/w, 1.0%. Gel permeation chromatography-high pressure analysis revealed that the esterification reaction yield was over 90% for each of the three natural rosins. Moreover, chromaticity coordinates (x,y), gloss factor (β), softening point (°C), and UVB aging test were applied to TRMPs. Modified natural rosins showed better results in the production of TRMPs. This is an important development and crucial step for sustainable TRMP production.

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INTRODUCTION

In recent years, the sensitivity to climate change and the goal of reducing carbon footprint have led to a reevaluation of production practices worldwide (Mitchell 2017). Reducing carbon footprint can be achieved by minimizing energy consumption in production and excluding unsustainable raw material sources from the production process. Instead of using petrochemical products that cause permanent damage to the environment, human health, and ecosystem balance, it is important to use natural sustainable products such as natural resins. The increase in the global demand for non-wood forest products has brought the necessity to sustain these resources. This can be achieved with more effective and efficient use of these products (Komut 2019).

Natural resin sources include pine resin, wood resin, and tall oil resin. Pine resin is the foremost source for resin products. It is obtained by applying various methods to live pine trees. Wood resin is produced by leaving the stump logs of fallen pine trees in the soil for approximately ten years after cutting, with the aim of preserving their bark and sapwood. During this period, the heartwood is enriched with resin. After the waiting period, the collected roots undergo certain pre-processing steps and are extracted with hexane to produce wood resin. Tall oil resin is obtained by distilling crude tall oil (CTO) (Abdel-Raouf and Abdul-Raheim 2018).

Pine resin is composed of a mixture of volatile (turpentine) and non-volatile (rosin) terpenes. Terpenes form the largest group of secondary metabolites in pine resin. Terpenes are derived from isopentenyl pyrophosphate (IPP). The biosynthesis of pine oleoresin involves volatile mono (C10) and sesquiterpene (C15) as well as non-volatile diterpenic (C20) fractions, which function as a volatile defense mechanism against their main predators (primarily bark beetles and associated pathogenic fungi) (Bohlmann and Keeling 2008).

Moreover, wood resin is a mixture obtained from the extraction of stump logs and roots, consisting of turpentine, pine oil, rosin, and tar. The production of wood resin is significantly different from other natural resin types in terms of the supply of raw materials and manufacturing process. It requires an industrial production approach (Angın 2020).

Tall oil is a commercially viable by-product of the kraft cooking process. The United States, Scandinavian countries, Russia, and China are the leading producers of tall oil (Baumassy 2014; Aro and Fatehi 2017). Tall oil consists of three main components: resin acids, fatty acids, and unsaponifiable matter (neutral compounds). Crude tall oil is primarily composed of fatty acids and long-chain resin acids, containing approximately 70 to 90% acidic structures (Abdel-Raouf and Abdul-Raheim 2018).

Rosin is the non-volatile solid part of natural resins. Rosin is semi-transparent, and its color varies from pale yellow to black. Rosin color is determined by parameters such as the type of source, time of production, production conditions, *etc*. Rosin is brittle, solid, crystalline, and amorphous at room temperature but softens and liquefies at high temperatures (Mahendra 2019; Bezzekhami *et al.* 2023a).

Irrespective of the origin of the natural resins, rosin is mainly composed of resin acids (90 to 95%). Residual components in the content of rosin are mainly from neutral compounds. Resin acids are diterpenic monocarboxylic acids with the general formula $C_{19}H_{29}COOH$ (Domanski *et al.* 1989). These resin acids can be referred to as abietic and pimaric type resin acids. Resin acids are not polymers like hydrocarbon resins, but their chemical structure consists of a mixture of molecules characterized by three fused six-carbon rings, double bonds varying in number and position, and a single carboxylic acid (Fiebach and Grimm 2000).

The most abundant resin acids in the chemical structure of rosin have an abietane skeleton and are known as abietic type resin acids (abietic, neoabietic, palustric, and levopimaric acid). The most important feature of this group resin acids is the different positions of the conjugated double bond system. The positions affect the chemical reactivity of these compounds and consequently, the applications of the products obtained from these compounds. The second most common resin acids in the chemical structure of rosin is pimaran-type resin acids. They include pimaric, isopimaric, and sandara-copimaric acids (González *et al.* 2010). Both abietic and pimaric type resin acids contain double bonds. Double bonds in abietic type resin acids represent conjugated double bonds. In pimaric type resin acids, the location of the double bonds and the position of the alkyl group attached to the 7th carbon differ from abietic type resin acids. The different positions of double bonds and alkyl groups in abietic and pimaric types of resin acids lead to distinct characteristics in modification reactions. Abietic type resin acids are subject to prompt isomerization and oxidation in the presence of oxygen, whereas pimaric type resin acids are more stable in these situations due to the lack of conjugation in their double bonds and the tetravalent bonding of the seventh carbon. Resin acids contain a free carboxyl group and carbon-carbon double bonds in their chemical structure. This formation allows them to readily react with other reagents to obtain various intermediate products (Sousa *et al.* 2019).

The reactivity of rosin is significantly influenced by the presence of the carboxyl group and the conjugated double bond in its structure. To enhance its stability and valuable properties, chemical modifications are often employed. Various methods, such as dimerization, isomerization, and disproportionation, can be utilized to improve the oxidative stability of rosin (Shiwei *et al.* 2009; Wang *et al.* 2009; Huang *et al.* 2015). One common modification involves esterification with alcohols or polyols and using different types of alcohols such as ethylene glycol, glycerol, and pentaerythritol, *etc*. This broadens the potential applications of rosin in different industries, as the modified rosin can be tailored to meet specific requirements based on its properties. The esterification of resin acids is industrially carried out at high temperatures (260 to 300 °C) and in the presence of various catalysts, such as metal oxides. Rosin pentaerythritol ester is a quaternary alcohol ester known for its enhanced water resistance, alkali resistance, and oxidation resistance, making it notably more stable. Consequently, it holds significant potential for various industrial applications, including its use as a component in pressure-sensitive adhesives, hot-melt adhesives, modifiers, and thermoplastic road marking paints (Gao *et al*. 2008).

Thermoplastic road marking paints (TRMPs) were first applied in the United States in 1958. The excellent results obtained after implementation gradually attracted an increasing number of countries to adopt this type of marking (Mirabedini *et al.* 2012). Thermoplastic road marking paints remain one of the most successful marking materials and continue to be widely applied in many countries. During application, the paint mixture is heated to a temperature of 180 to 200 ℃ within the extrusion process and is then applied to the road surface while in a hot state. After cooling and solidifying, TRMPs complete their adhesion to the road surface. To achieve low surface slip and the necessary initial reflectivity, anti-skid materials and glass beads are scattered onto the paint surface. Due to their high durability, thermoplastic markings are widely used in areas with heavy traffic, such as pedestrian crossings and stop bars (Xu *et al.* 2021). In order to prevent the road paints from melting in high temperatures during hot summer days, paint production utilizes modified rosin with a softening point exceeding 100 °C, as mandated by the standard (TS EN 1871). This measure effectively mitigates any potential adverse consequences. The main objective of this study was to evaluate pentaerythritol ester rosins as binders in the production of TRMPs. There has been almost no study focused on the conversion of wood rosin to TRMP following esterification with pentaerythritol.

EXPERIMENTAL

Materials

Pinus pinaster resin rosin was used as pine resin rosin. The wood rosin was supplied from IVA Resin Biomass Industry Inc., and the tall oil rosin was supplied from Diper Chemistry Industry and Trade Inc. For the esterification process, pentaerythritol purity ≥ 99.9% (Sigma-Aldrich, St. Louis, USA), (1,1-Di-tert. -butyl)-4-hydroxyphenyl) methyl) ethylphosphonate) (Irganox 1425, BASF, CAS Number: 65140-91-2), TBM-6 (4,4'-Thiobis(2-tert-butyl-5-methylphenol)) (358.54 g/mol, Sigma-Aldrich) chemicals were obtained. The production of modified thermoplastic road marking paints was carried out with the support of SİGNATEKMA Paint and Signaling Industry and Trade Inc. (Turkey).

Esterification of Natural Rosins with Pentaerythritol

The pentaerythritol ester of natural rosin is one of the most preferred modified ester rosin products in the production of TRMPs. The esterification studies of pentaerythritol and rosins aimed to develop modified rosin products with high oxidation resistance and thermoplastic properties. The optimum synthesis conditions have been determined with a pentaerythritol/rosin mol/mol ratio of 1/1, TBM-6/rosin at 1.0% w/w, and Irganox 1425/rosin at 0.5% w/w. The esterification reaction was carried out for three different natural rosin samples separately. After adding rosin to the system and adjusting the mechanical stirrer and nitrogen gas, the reaction was initiated with the opening of the cooling system. The reaction took place in a 1L, 4-necked reaction flask. Upon adding rosin to the reaction flask, the temperature was gradually increased to 210 °C. As the temperature was increased, the stirrer speed was increased to prevent oxidation. When the temperature reached the 120 °C range, antioxidant additive (TBM-6) was added into the system, and the temperature was raised to the range of 260 to 270 °C. After reaching temperatures of 218 to 220 °C, pentaerythritol alcohol was added to the system to ensure homogeneous mixing with rosin. Following the homogeneous mixing of pentaerythritol and rosin, when the temperature approached 240 °C, a catalyst (Irganox 1425) was added. The temperature range of 270 to 275 °C was determined as ideal for the esterification of pentaerythritol with natural rosins. The reaction time varied depending on the type of rosin source but was generally determined to be in the range of 6 to 8 hours.

While the reaction was ongoing, the acid number of the reaction product inside the reaction flask was measured every 2 hours based on the ASTM D 465-05 standard. At the end of the reaction, FT-IR spectra were obtained to determine the stage of esterification reaction. Additionally, the softening point of the final product after the reaction was determined according to ASTM E 28-99 standard.

Production of Thermoplastic Road Marking Paints from Pentaerythritol Ester Rosins

The production of TRMPs from the esterified rosins was carried out on-site at the factory located in Izmir/Torbalı with the support of SİGNATEKMA Inc. Alongside the synthesized ester rosin, TRMPs production was conducted using modified rosin actively used by SİGNATEKMA Inc. The list of binders used in TRMPs production is provided in Table 1.

Table 1. Binders Used in the Production of Thermoplastic Road Marking Paint

Binder	Code
Pentaerythritol ester pine resin rosin	PEK
Pentaerythritol ester tall oil rosin	TOPEK
Pentaerythritol ester wood rosin	WRPE
Standard modified rosin	STD

The brand and type information of the inputs included in the formulation content has not been disclosed due to confidentiality requirements. The preparation formulation of the TRMPs is described in Table 2. The formulation was transformed into a flowable thermoplastic paint by continuously stirring at approximately 200 °C on a magnetic mixer heater. The transformation of the thermoplastic paint into a liquid and flowable state made it suitable for testing and analysis.

Table 2. Formulation to Produce Thermoplastic Road Marking Paint

Order	Ingredients	% Additive	Preparation
1	Pigment (TiO_2)	10	The specified amount of pigment was first added to the working container.
2	Filler (talc, $CaCO_3$)	40	Subsequently, the specified amount of filler material was added.
3	Glass Beads	20	The specified amount of glass beads was added to the working container.
4	Binder (pentaerythritol ester rosin)	20	The direct contact of heat with the binding resin was prevented by adding the binding resin to the TRMP formulation until the end.
5	Plasticizer (Vaks)	10	It was added last to ensure the homogeneity of the paint mixture

Fourier Transform Infrared (FT-IR) and Thermogravimetric Analyses (TGA)

The FT-IR analysis of modified and unmodified rosins was conducted using a Perkin-Elmer (Model: Frontier) instrument from the USA (Waltham, MA). Infrared spectra were acquired employing the attenuated total reflection (ATR) technique. Fourier transform infrared spectra were recorded in the wavelength range of 4000 to 5000 cm^{-1} with a resolution of 4 cm^{-1}.

Thermogravimetric analysis was conducted using a Perkin Elmer instrument (Model TGA 4000). In addition, 4 to 10 mg of the modified/unmodified rosin sample was taken and placed in the crucible of the device separately. The analysis was carried out under a nitrogen atmosphere, starting at 30 °C and increasing at a rate of 10 °C per minute until reaching 800 °C. When the temperature reached 800 °C, the mass loss was monitored until completion, and the samples were held at this temperature (Zhou *et al.* 2020).

MALDI ToF-MS and GPC-HPLC Analyses

The MALDI-ToF-MS analysis was performed using a Bruker Microflex LT model instrument. Typically, for modified/unmodified rosin samples, a saturated matrix solution was prepared. During the matrix solution preparation, the sample was dissolved in a solvent containing TA (33% Acetonitrile, 0.1% TFA), and the matrix solution was mixed with the sample in equal volumes. The mixture was pipetted onto the target (0.5 to 1 µL), dried at room temperature, and prepared for analysis.

Table 3. Parameters of GPC-HPLC Analysis

Column	2 × Jordi Gel DVB 500A (300 mm × 7.8 mm), guard column, 50 × 7.8 mm
Solvent	THF (1% dissolved in acetic acid)
Flow rate	0.8 mL/min
Temperature	40 °C
Injection volume	30 µl
Dedector	ELSD, HPLC nebulizer, 40 °C, air pressure: 3.5 bar

The purpose of the GPC-HPLC analysis is to elucidate the chemical content of rosin before advanced modification processes and to reveal the structural changes that occur after the modification. The analysis parameters are listed in Table 3. The analysis was applied in splitless mode, with an analysis time of 28 min. The samples to be analyzed were prepared by dissolving 4 mg of the sample in 4 mL of solvent (tetrahydrofuran).

Acid Number and Softening Point Standard Tests

The acid number values of modified/unmodified rosins were determined according to ASTM D 465-05. For each rosin sample, 4 ± 0.05 g of the sample were taken into a beaker, and according to the relevant standard, 25 mL of toluene and 75 mL of isopropyl alcohol were added. Following this, the sample was homogenized using an ultrasonic bath treatment to ensure the complete dissolution of the sample. A few drops of phenolphthalein indicator solution (obtained by dissolving 1 g of phenolphthalein in 100 mL of CH_3OH) were added to the homogenous sample. Then, it was titrated with a pre-prepared 0.5 N alkali standard solution (KOH dissolved in CH_3OH) using the internal indicator method. The titration was concluded when a constant color change towards pale pink was observed while titrating the sample with the titration solution in the graduated burette. The acid value in rosin samples was determined using Eq 1,

$$\text{Acid value: } A \times N \times 56.1 / B \tag{1}$$

where A is volume of titration solution consumed during titration (mL), N is normality of the titration solution (g/L), and B is weight of the analyte (g).

The determination of the softening point was conducted in accordance with ASTM E 28-99 standard. For the softening point determination, a quantity of rosin was taken into a small beaker and completely liquefied on a flat heater.

The liquefied rosin sample was carefully transferred to a ring-shaped apparatus made of stainless steel, and it was allowed to cool and solidify. Once solidified, the samples were placed on the softening point apparatus with balls on top. Subsequently, the apparatus was transferred into a 1 L glass beaker filled with distilled water. The glass beaker was placed on a stirred flat heater, and a contact thermometer was arranged to monitor the temperature inside the beaker. As the temperature of the water increased, the solidified rosin samples within the rings softened, and with the softening of rosin, the balls on top of them fell onto the plate at the bottom of the softening point apparatus. The moment the sample fell onto the plate, the temperature was recorded from the thermometer. The experiments were conducted twice, and the average softening point (°C) values were calculated.

Thermoplastic Road Marking Paints' Analyses

Various tests specified by standards were applied to the road marking materials produced by SİGNATEKMA Inc. The tests were carried out as specified in the TS EN 1871 Road Marking Materials - Physical Properties Standard.

Chromaticity coordinates and gloss factor

The relevant test was applied to TRMPs according to TS EN 1871. For white-colored paints, it was checked whether they were within their own color spaces as required by the standard. The completed formulation of the paint samples inside small paint cans in powder form was melted in an oven with continuous stirring at approximately 150 ℃ for about 40 min. The homogenized liquid paint samples were continuously stirred for 6 h with a spatula, maintaining a constant temperature of approximately 180 ℃. During the continuous stirring process, a small amount of paint sample was taken from each paint container every hour and poured onto separate rubber molds for each paint production. The x, y coordinates, and β (gloss factor) values of each prepared mold were measured the next day. The stages of preparing samples for the measurement of chromaticity coordinates and gloss factor are illustrated in Fig. 1.

Fig. 1. Preparation of chromaticity coordinates and gloss factor measurement for TRMPs samples

Measurements with the spectrophotometer were taken from three different locations on each mold, and average values were recorded. For white TRMPs, the gloss factor value ($\Delta\beta$) before heat stability should have been ≥ 0.65 for LF3, ≥ 0.70 for LF4, and ≥ 0.80 for LF6 class. After the heat stability test, the difference value with the first heating should not have exceeded 0.10.

UVB aging test

For each paint sample to be analyzed in the UVB aging test, samples were prepared to form a film on aluminum panels with dimensions of 150 × 75 × 0.60 mm, according to TS EN 1871, with a thickness of 400µm ± 35µm in a wet state. The samples were subjected to the test for 168 hours with cycles consisting of 8 hours of irradiation at 60 °C ± 2 °C under lamp type II (UVB-313) and 4 hours of condensation at 50 °C ± 2 °C, according to TS EN ISO 4892-3. After aging with UV, the difference in gloss factor should be classified as shown in Table 4.

Table 4. Classes of Difference in Gloss Factor after UVB Aging

Color	Class	$\Delta\beta$
White and Yellow	UV 0	Unsearchable (Non-standard)
	UV 1	≤ 0,05
	UV 2	≤ 0,10

Softening point analyses

The determination of the softening point was conducted according to TS EN 1871. The softening point class for TRMPs should be SP3 (95 °C ≤ SP3 < 110 °C).

RESULTS AND DISCUSSION

FTIR Results

The FT-IR spectra of unmodified and modified rosins are presented in Fig. 2.

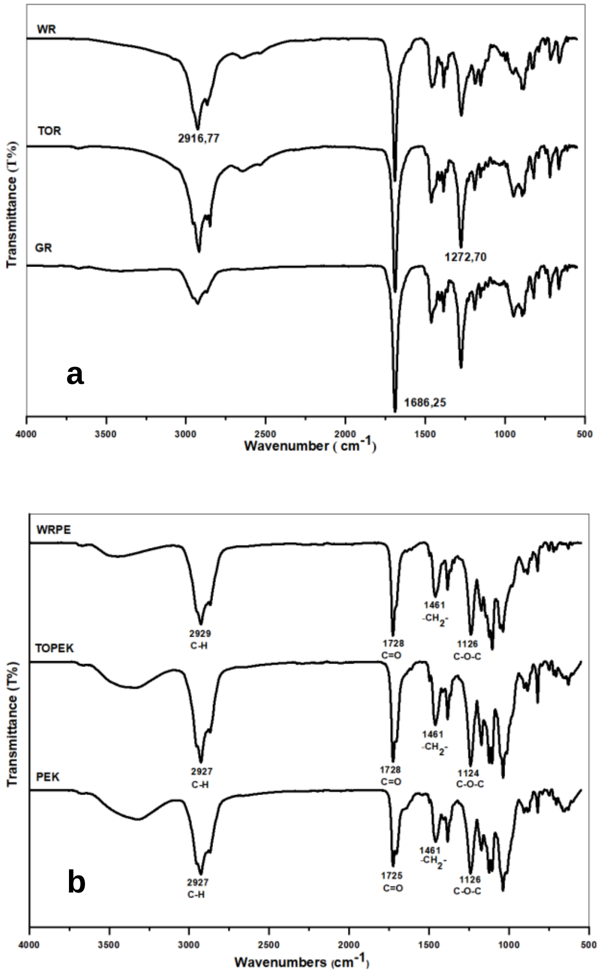

Fig. 2. FT-IR analyses of unmodified (a) and modified rosin (b) samples

The FT-IR analysis revealed that the spectrum images of rosins were very similar to each other. This indicates that the chemical structures of the natural rosins were closely alike. The spectra in the FT-IR analysis of natural rosins should be divided into four regions: (a) the OH region located between 3700 and 3200 cm^{-1}; (b) the carbonyl region between 1800 and 1550 cm^{-1}; (c) the CH region between 3200 and 2400 cm^{-1}; and (d) the fingerprint region between 1550 and 600 cm^{-1} (Kızıl *et al.* 2002; Azemard *et al.* 2014).

In Fig. 2, FT-IR spectra of unmodified rosins observed in the range of 2916.8 cm^{-1} identified as aliphatic C-H bonds within the structure. They exhibited the strong stretching vibration modes of C-H for both the methyl and methylene groups due to the three-ring hydrocarbon structures specific to these diterpenes (Favvas *et al.* 2015). The sharp peak at 1686.2 cm^{-1} was identified as C = O stretching vibration. The peak is a characteristic feature of the binding of carboxylic acids (De Souza Correa *et al.* 2018).

The peak at 1272.7 cm^{-1} is attributed to C-O-C stretching vibrations within the -COOH group (Wang *et al.* 2016). When the FT-IR spectra are examined, it is observed that the chemical structures of the natural rosins obtained from three different natural sources are nearly identical.

In the FTIR spectrum of the synthesized pentaerythritol ester rosins (PEK, TOPEK, and WRPE), the peak observed at 1725 and 1728 cm^{-1} had been identified as the ester carbonyl peak (C = O) (Bezzekhami *et al.* 2023b). In the modified rosin samples, one of the most important peaks, the carboxylic acid carbonyl peak in the resin acid, had been transformed into the ester carbonyl peak after the ester reaction, indicating that the reactions had been successfully carried out (Xu *et al.* 2019). In addition, the peak observed at 1686.2 cm^{-1} in natural rosin had shifted to 1700 cm^{-1}. The peak observed in the range of 2927 to 2629 cm^{-1} corresponds to the C-H bonds within the structure. The peak observed at 1461 cm^{-1} arises from the scissoring vibration within the pentaerythritol ester structure, and the peak observed at 1124 and 1126 cm^{-1} corresponds to C-O-C stretching vibrations.

TGA Results

The TGA experiment measured weight loss concerning time and temperature, as illustrated in Fig. 3.

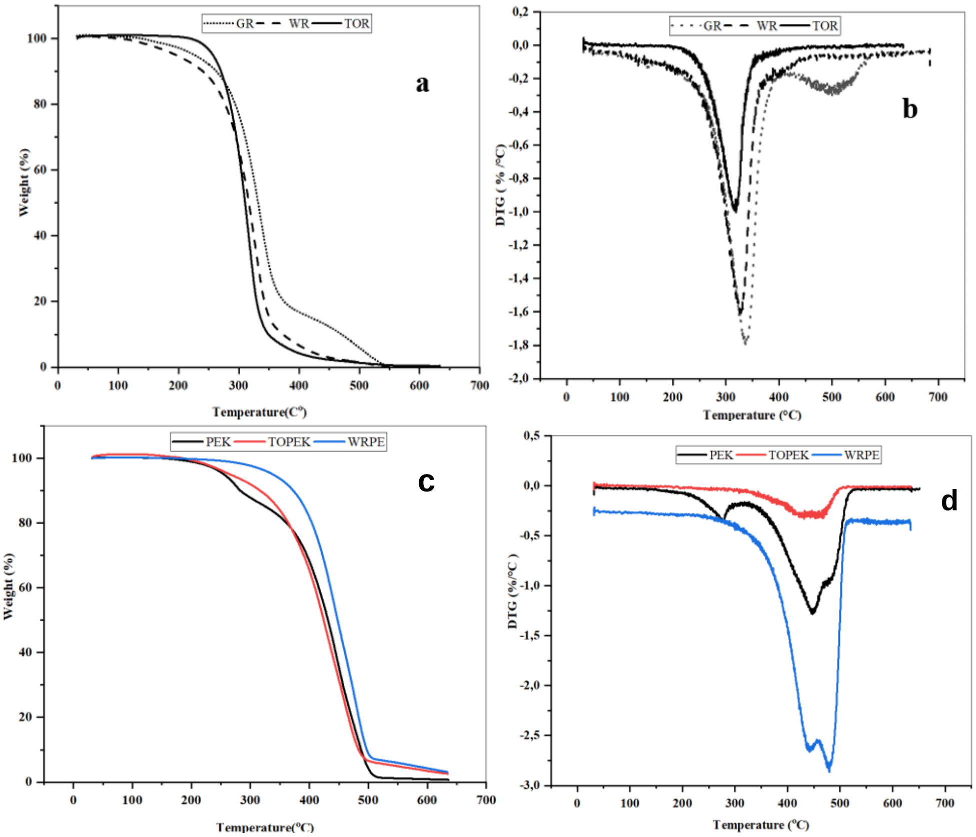

Fig. 3. TGA and DTG curves of unmodified (a, b) and modified rosin (c, d) samples

The TGA curves revealed a three-step process in the thermal degradation of all materials. In the TGA analyses of unmodified rosins, the initial step was marked by a flat curve, indicating consistent sample mass (Coats and Redfern 1963; Pavon *et al.* 2020). The second stage, starting at approximately 250° C, showed a sudden shift in mass loss accompanied by an increase in the degradation rate. Lastly, temperatures exceeding 450 °C exhibited minor weight fluctuations with a tendency to stabilize. According to DTG curve, the GR sample had the highest decomposition temperature at 336.0 ℃, whereas the TOR sample exhibited the lowest temperature at 317.4 ℃.

TGA analyses revealed significant distinctions between pentaerythritol ester rosins and unmodified rosins. In the case of modified rosins, the initial stage exhibited a sustained sample mass, indicated by a prolonged flat curve. Subsequently, during the second stage, a sudden mass loss occurred at around 345 ℃. Finally, as temperatures surpassed 600 °C, minor weight variations were noted. According to the DTG curve of the pentaerythritol ester rosins, the TOPEK sample demonstrated the highest decomposition temperature at 445 °C, while the WRPE sample exhibited the lowest at 436 °C. When TGA results were examined, it was observed that the decomposition temperature noticeably increased after esterification of rosin with pentaerythritol. Thus, the esterification process enhanced thermal stability, contributing to the material becoming more resistant to higher temperatures. Higher decomposition temperatures can increase the resistance of material to heat, generally improving its performance in thermal applications and under conditions requiring durability. The temperature during the production of TRMPs is around 200 °C. It is crucial for the material not to oxidize or decompose at these temperatures, which is a critical parameter for the final product quality.

The findings indicated that pentaerythritol ester improved thermal stability by postponing the degradation/decomposition process to higher temperatures. The behavior was attributed to the intrinsic thermal characteristics of modified rosins, which exhibited greater stability compared to GR due to its modification through esterification. The same phenomenon was observed in the studies conducted by Aldas *et al*. (2020) and De La Rosa-Ramírez *et al*. (2020).

MALDI ToF-MS Results

The MALDI-ToF MS analysis for modified and unmodified rosin samples is presented Table 5. Rosins are a mixture of small molecules consisting of different isomers, commonly known as resin acids. The chemical structure of a resin acid typically comprises cyclic rings, conjugated double bonds, and a carboxylic group. These features provide numerous potential pathways for structural modifications in rosins. Despite being composed of cyclic ring structures, they remain anti-aromatic, making them amenable to chemical reactions and modification (Mitchell *et al.* 2018).

The compounds within the chemical structure of rosin are divided into two main types: abietic and pimaric acid. The most common structures in the chemical composition are abietic acid and its isomers. The molecular weight of abietic acid is 302.44 g/mol. According to the results obtained from mass analysis of rosins, it has been confirmed that abietic acid is predominant in the chemical composition.

Table 5. MALDI TOF-MS results

Rosin	MS Analysis Report (g/mol)
Gum Rosin (GR)	302.342
Tall Oil Rosin (TOR)	302.153
Wood Rosin (WR)	302.310
Gum Rosin Pentaerythritol Ester (PEK)	430.545
Tall Oill Rosin Pentaerythritol Ester (TOPEK)	444.552
Wood Rosin Pentaerythritol Ester (WRPE)	421.889

Tall oil rosin contains a lower amount of resin acids compared to other types of rosins. In general, tall oil comprises mainly of fatty acids (30 to 60%, mainly oleic acid and linoleic acid), resin acids, and a small amount of unsaponifiable substances (5 to 10%, high molecular weight alcohols, sterols, and other alkyl hydrocarbon derivatives) (Biermann 1996; Uusi-Kyyny *et al.* 2017; Vevere *et al.* 2020).

In the mass analysis results of pentaerythritol ester rosins, a noticeable increase in molecular weight was observed. The increase stemmed from the ester reaction between the free carboxylic acid and pentaerythritol, resulting in a new structure. The molecular weight of the newly formed structure was calculated and determined to be approximately 420.58 g/mol. Mass spectrometry analysis revealed the masses of PEK, TOPEK, and WRPE as 430.545 g/mol - [$-CH_3$] + [Na^+], 444.552 g/mol + [Na^+], and 421.889 g/mol + [H^+], respectively.

GPC-HPLC Results

The results of GPC-HPLC analysis for natural rosins and pentaerythritol ester rosins are presented in Tables 6 and 7, respectively. Through GPC-HPLC analysis of natural rosins, GR was identified as the rosin sample with the highest concentration of abietic acid, at 96.5%. Meanwhile, TOR was determined as the rosin sample with the least presence of abietic acid, at 92.3%. Abietic acid and its isomers were identified as the resin acids present in the highest proportion in the content of rosin in the 22.68 to 22.70 minute range. In addition to these results, structures with molecular weights higher than resin acids were detected in the rosin within the 20.81 and 21.33 minute range.

Table 6. The GPC-HPLC Analysis Results for Rosins

Rosin	Peak	Retention Time (RT, min)	Area %
GR	1	21.33	3.48
	2	22.68	96.5
WR	1	21.35	3.59
	2	22.70	95.4
TOR	1	20.81	2.31
	2	21.41	1.72
	3	22.70	92.3

The purpose of conducting GPC-HPLC analysis is to determine the efficiency of the esterification reaction. After the esterification of natural rosins with pentaerythritol, it was determined that mono-, di-, tri-, and tetra-ester structures were formed (Table 7). Upon examination of the percentage areas of these ester structures, it was observed that the -mono, di- and tri-ester structures were more predominant, and the presence of tetra- -ester structures was also detected. The percentages for PEK, WRPE, and TOPEK were determined as 92.6%, 93.9%, and 92.8%, respectively. The analysis results indicated that the esterification reaction successfully occurred with high efficiency. Pentaerythritol belongs to the class of polyhydric alcohols, as it contains four hydroxyl (-OH) groups in its chemical structure. The presence of numerous hydroxyl groups makes it highly reactive for esterification reactions. During the esterification reaction between the free carboxyl group (-COOH) in the structure of rosin and the hydroxyl group in the alcohol structure of pentaerythritol, each reaction results in the formation of an ester bond between -COOH and -OH groups, accompanied by the release of one mole of H_2O. The four separate hydroxyl groups in the structure of pentaerythritol allow the formation of four different ester bonds in esterification reactions (Hardhianti *et al*. 2021). This condition demonstrates the effectiveness of the reaction by increasing the esterification efficiency.

Table 7. The GPC-HPLC Analysis Results for Pentaerythritol Ester Rosins

PEK				WRPE			TOPEK		
No	RT (min)	Structure	Area %	RT (min)	Structure	Area %	RT (min)	Structure	Area %
1	19,304	Large molecules	1,159	19,071	Large molecules	3,981	19,337	Large molecules	2,605
2	19,771	Tetra ester	3,520	19,692	Tetra ester	13,533	19,854	Tetra ester	5,667
3	20,132	Tri-ester	25,806	20,153	Tri-ester	38,215	20,164	Tri-ester	28,385
4	20,861	Di-ester	42,134	20,883	Di-ester	35,717	20,893	Di-ester	43,308
5	22,052	Mono-ester	21,155	22,048	Mono-ester	6,403	22,052	Mono-ester	15,450
6	22,668	Resin acids	5,088	22,663	Resin acids	2,151	22,665	Resin Acids	3,757

Acid Number and Softening Point Standard Test Results

The acid and softening point values of natural rosin samples before and after the esterification reaction are presented in Table 8. Before the esterification reaction, the acid values of natural rosin were high due to the presence of free -COOH in their chemical structures. As the esterification reaction progressed, acid values were calculated every two hours according to ASTM D 465-05, and the reactions were terminated when the acid values fell below 15.0 mg KOH/g. As the acid value decreased, the thermoplastic character of material increased, and consequently, the esterification efficiency also improved. It was observed that, as the esterification reaction progressed, the acid value of rosin gradually decreased. The reduction occurred more rapidly in the initial hours of the reaction.

Table 8. Acid Number (mg KOH/g) and Softening Point (°C) Results of the Modified and Unmodified Rosins

Rosin	Acid number (mgKOH/gr)	Softening point (°C)
GR	157.09	77.36
TOR	176.00	75.45
WR	154.00	78.80
PEK	12,69	81.00
TOPEK	11,24	76.00
WRPE	7,77	78.00

In all types of natural rosins, an increase in molecular weight was observed after the esterification reaction, leading to an increase in the softening point. The presence of a significant amount of tetra-ester structures in the esterified rosin structure contributes to an increase in the softening point (Hardhianti *et al*. 2021). However, since only a small amount of tetra-ester structures was observed in the study, a noticeable increase in the softening points of the synthesized products was not observed. Additionally, before the esterification reaction, the softening point and acid value of natural rosins, as well as the type of resin from which rosin was obtained and the extraction method, play a crucial role. Many parameters, such as the storage conditions of pine resin, the type of tree used for the extraction of wood resin, the type of chemical used in extraction *etc.*, have a significant impact on the softening point and acid value (Mahendra 2019).

Thermoplastic Road Marking Paints' Analyses Results

Chromaticity coordinates and gloss factor

The results regarding chromaticity coordinates and gloss factor analysis of TRMPs are presented in Table 9. The *x*, *y*, and *β* values of TRMPs were measured according to the TS EN 1871 standard, and the classes were determined both before and after heat stability. It was determined that three different paints produced from natural ester rosins were produced within the TS EN 1871 standard.

The *β* factor is typically affected by the TiO_2 content in the coating and the surface's ability to reflect properly at a 45° angle. In this case, all samples had identical TiO_2 pigment content (Mirabedini *et al.* 2020). As anticipated, the color change measurements following the heat stability test indicated superior heat stability in samples based on rosin ester compared to those containing hydrocarbon resin.

Table 9. Chromaticity Coordinates and Gloss Factor Analysis Results of TRMPs

TRMP	PATERN						HEAT STABILITY	
							Before	After
	1	2	3	4	5	6	*β**	
PEK	x:0.3434 y:0.3427 β:79.25	x:0.3257 y:0.3445 β:77.61	x:0.3268 y:0.3459 β:77.01	x:0.3255 y:0.3521 β:73.50	x:0.3316 y:0.3528 β:72.77	x:0.3307 y:0.3513 β:72.54	LF4	LF4
TOPEK	x:0.3272 y: 0.3450 80.49	x:0.3252 y:0.3446 β:80.09	x:0.3282 y:0.3471 β:75.94	x:0.3281 y:0.3480 β:74.71	x:0.3290 y:0.3491 β:74.48	x:0.3307 y:0.3509 β:73.01	LF6	LF6
WRPE	x:0.3383 y:0.3557 β:77.41	x:0.3391 y:0.3560 β:75.65	x:0.3403 y:0.3570 β:72.49	x:0.3401 y:0.3571 β:71.69	x:0.3406 y:0.3576 β:69.59	x:0.3405 y:0.3575 β:68.49	LF4	LF4
STD	x:0.3292 y:0.3465 β:80.40	x:0.3269 y:0.3453 β:80.08	x:0.3283 y:0.3468 β:78.33	x:0.3269 y:0.3456 β:75.68	x:0.3288 y:0.3471 β:74.41	x:0.3276 y:0.3468 β:71.85	LF6	LF6

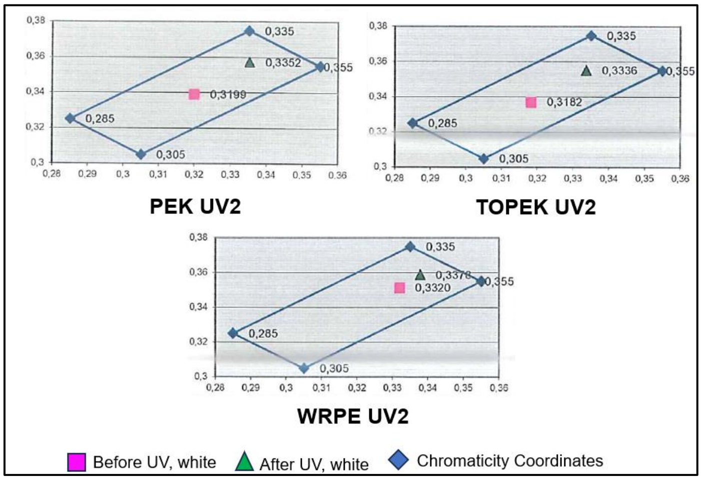

Fig. 4. Chromaticity coordinate graphs of TRMPs produced with pentaerythritol ester rosins, before and after UVB aging tests

UVB aging test

The results of the UVB aging test are presented in Fig. 4. The UVB aging test was conducted at the General Directorate of Highways Physics Laboratory in Ankara, Türkiye. The test was applied to all paints, except for the commercially available standard ester rosin-based thermoplastic road marking paint (STD). Standard values were obtained for all paints developed within the scope of the study. The results support the development of sustainable, environmentally friendly TRMPs using various natural modified rosins.

Softening point (T_{sp})

The softening points TRMPs are presented in Table 10. According to TS EN 1871, the softening point class for TRMPs should be SP3 (95 °C ≤ SP3 < 110°C). Softening point values were determined within the standard for all TRMPs. The adjustment of the softening point can be achieved through the selection of an appropriate amount of resin and plasticizer. The study results have supported the use of the right quantity and characteristics of resin and plasticizer in TRMPs preparation and application (Voznyi *et al.* 2015; Mirabedini *et al.* 2020).

Table 10. Softening Points of TRMPs

Softening Point (T_{sp}), °C			
STD	TOPEK	WRPE	PEK
104	106	110	108

CONCLUSIONS

1. In the Fourier transform infrared (FT-IR) analysis of unmodified rosins, the C = O double bond was observed at 1686.2 cm^{-1}. After the esterification reaction, the peak shifted towards the range 1725 to 1728 cm^{-1}. The shift indicated that the esterification reaction successfully occurred.
2. The esterification reaction efficiencies were achieved as follows: pentaerythritol ester pine rosin (PEK) (92.6%), pentaerythritol ester wood rosin (WRPE) (93.9%), and TOPEK (92.8%) by gel permeation chromatography – high performance liquid chromatography (GPC-HPLC) analyses.
3. The increased thermal resistance of natural rosins after the esterification reaction was supported by thermogravimetric analysis (TGA). Among the unmodified rosins, the pine rosin (GR) sample exhibited the highest decomposition temperature at 336.0 °C, while the tall oil rosin (TOR) sample had the lowest at 317.4 °C. Regarding the pentaerythritol ester rosin samples, the pentaerythritol ester tall oil rosin (TOPEK) demonstrated the highest decomposition temperature at 445.32 °C, whereas the pentaerythritol ester wood rosin (WRPE) sample showed the lowest at 436.0 °C.
4. All thermoplastic road marking paints (TRMPs) were obtained with standard values in terms of chromaticity coordinates and heat stability. According to results of TRMPs, PEK and WRPE were determined as LF4 class, and TRMP and TOPEK were determined as LF6 class. Moreover, TRMPs produced with modified natural rosins were standardized with UV2 class based on the UVB aging experiment results.

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APPENDIX

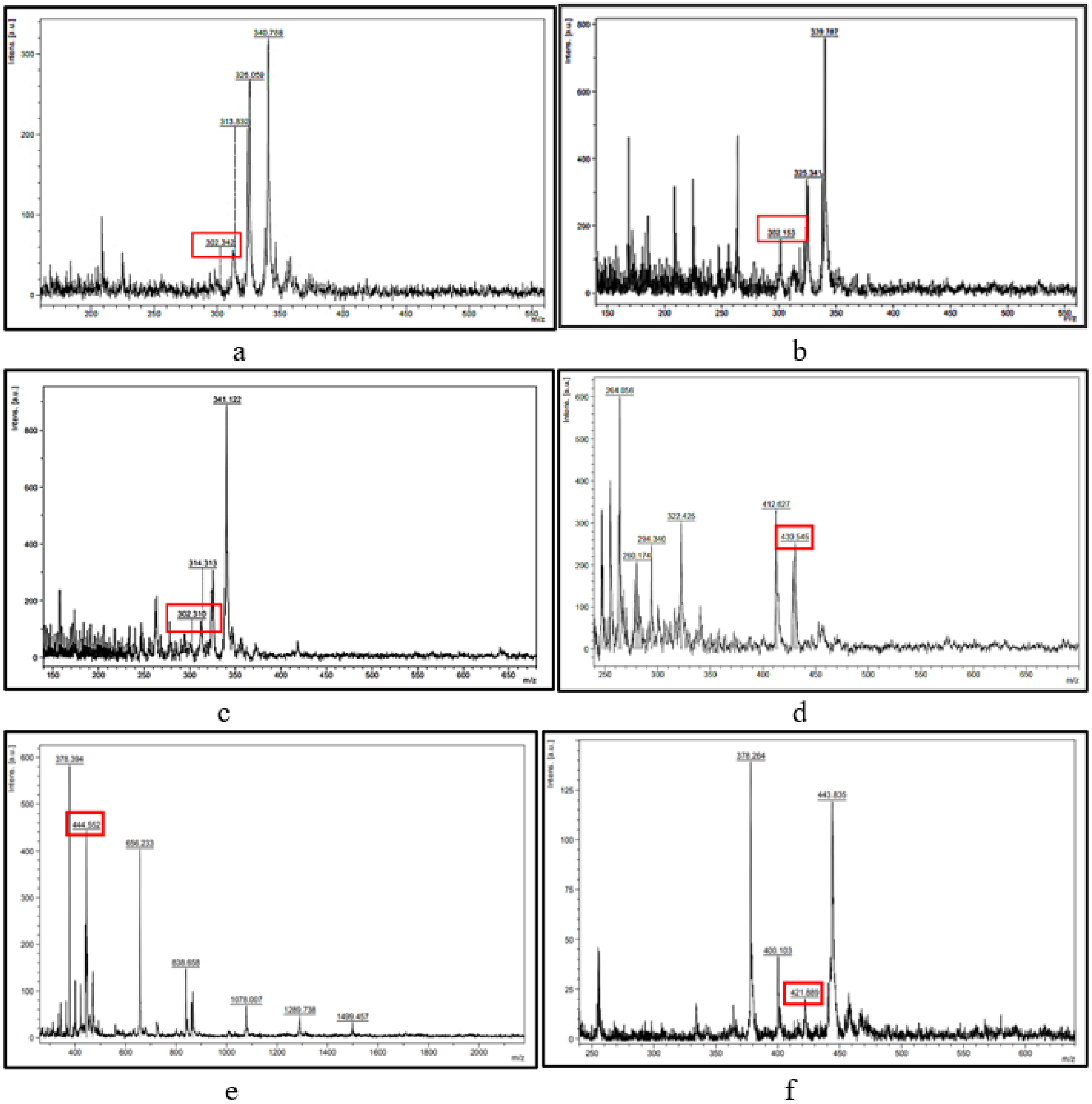

Fig. S1. Unmodified and modified rosin examples subjected to MALDI TOF-MS Analysis: a: pine rosin, b: tall oil rosin, c: wood rosin, d: pine rosin pentaerythritol ester, e: tall oil rosin pentaerythritol ester, f: wood rosin pentaerythritol ester

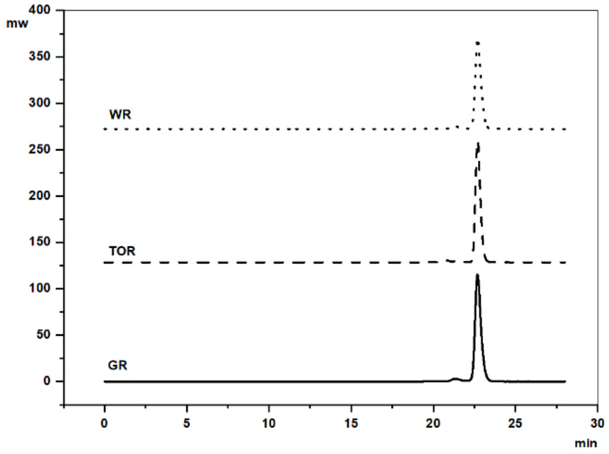

Fig. S2. GPC-HPLC spectrum of unmodified natural rosins

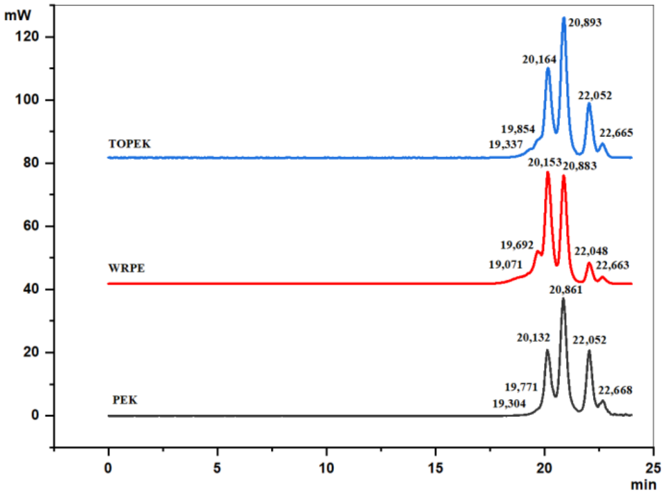

Fig. S3. GPC-HPLC spectrum of modified natural rosins