

This document is the accepted manuscript version of the following article:
dos Santos, S., Kakar, M. R., Partl, M. N., & Poulikakos, L. D. (2022). Thermal aging of bitumen and biorejuvenator blends: triglyceride versus free fatty acids. Journal of Materials in Civil Engineering, 34(7), 04022134 (10 pp.). [https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0004258](https://doi.org/10.1061/(ASCE)MT.1943-5533.0004258)

Thermal aging of bitumen and bio-rejuvenator blends: Triglyceride versus free fatty acids

Salomé dos Santos, Muhammad Rafiq Kakar*, Manfred N. Partl and Lily D. Poulikakos

Affiliation Statement:

Salomé dos Santos

Empa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600

Dübendorf, Switzerland.

Email: salome.rabaca.santos@gmail.com

Muhammad Rafiq Kakar

*Corresponding author:

Empa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600

Dübendorf, Switzerland, muhammad.kakar@empa.ch

Department of Architecture, Wood and Civil Engineering, Bern University of Applied Sciences (BFH),

Pestalozzistrasse 20, 3400 Burgdorf, Switzerland, muhammad.kakar@bfh.ch

Manfred N. Partl

Empa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600

Dübendorf, Switzerland.

Email: manfred.partl@bluewin.ch

Lily D. Poulikakos

Empa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600

Dübendorf, Switzerland.

Email: lily.poulikakos@empa.ch

Abstract. When added to aged bitumen, oil-based rejuvenators are expected to restore its original properties to some degree. The extent of the rejuvenation depends on the composition of the oils. In this study, the effect of individual components of vegetable oils on blends with bitumen was investigated. 5 and 10 wt% of two free fatty acids, oleic acid and linoleic acid, and one triglyceride, triolein, was blended with bitumen and thereafter the blends underwent thermal aging at high temperatures under air in a ventilated oven. The fatty acids and triglyceride are referred to as rejuvenators in this context. Upon thermal aging, the free fatty acids did not produce any effect or were much less effective in decreasing the complex shear modulus (stiffness) of bitumen as compared with the triglyceride. One reason for this result may be the favorable chemical changes of the triglyceride at high temperatures compared with the free fatty acids. Above all, this study provides basic

knowledge to demonstrate the importance of the chemical composition of vegetable oils that are selected as bitumen rejuvenators, specifically when targeting long-term stability of the blends.

Keywords: Bitumen; Rejuvenators; Recycling; Fatty acids; Triglycerides; Rheological properties; Thermal stability

Introduction

Bitumen is used in large amounts worldwide for several applications such as asphalt pavements. It is obtained from the distillation of crude petroleum and is a complex mixture of hydrocarbon molecules. It ages due to different chemical and physicochemical processes such as loss of volatiles, oxidation, and polymerization and, consequently, loses its mechanical, rheological, cohesive and adhesive properties (Marsac et al. 2014; Petersen and Glaser 2011; Lesueur 2009). In the context of sustainable construction and energy savings, recycling of aged bitumen can contribute to the re-use of aged asphalt by reducing fatigue, low temperature cracking and moisture sensitivity.

It is well-recognized that the recycling process must result in the restoration or alteration of the properties of aged bitumen including its rheological properties. The blending of unaged soft bitumen with aged bitumen is one way to restore or alter its properties (Poulikakos et al. 2014). Another way of recycling uses rejuvenators which must be chemically compatible with aged bitumen to obtain good blending that lasts over time. By using rejuvenators, the necessity of blending with unaged bitumen is reduced. This is particularly interesting from the perspective of reducing material costs as bitumen is the most expensive component in asphalt pavements. For environmental and economic reasons, post-consumer substances and cost-effective bio-based materials such as (waste) vegetable oils have been studied (Hugener et al. 2014; Yu et al. 2014; Zaumanis et al. 2014; Nahar et al. 2014; Zaumanis et al. 2015; Huang et al. 2015).

Vegetable oils are complex mixtures composed of triglycerides extracted from plants. Triglycerides are molecules composed of three chains of (free) fatty acids covalently connected through ester bonds to a glycerol moiety. The fatty acid chains can be saturated or unsaturated depending on the number of double bonds. The unsaturated bonds are more prone to oxidation, degradation and polymerization. Depending on the degree of refining the vegetable oils may contain free fatty acids among other components. Free fatty acids are more susceptible to oxidation than esterified fatty acids. Vegetable oils are characterized in relation to the fatty acids that constitute the triglycerides. The chain length and the degree of unsaturation vary greatly depending on the type of oil; therefore, the carboxylic acids commonly found in vegetable oils are present in different proportions.

The most commonly found saturated fatty acids are palmitic (16:0) and stearic (18:0). Many vegetable oils contain at least a small amount of each saturated fatty acid. Similarly, oleic acid (18:1) is a monounsaturated carboxylic acid that is found in large quantities in most vegetable oils and fats. Many oils and fats contain considerable amounts of linoleic acid (18:2), and some contain linolenic acid (18:3) (Mattson and Volpenhein 1963; Bockish 1998).

Original vegetable oils and waste vegetable oils coming from food frying have shown improvement in different asphalt or bitumen properties (Cavalli et al. 2018). Asli et al. (2012) showed that penetration, softening point and viscosity of bitumen can be recovered by using frying vegetable oil. Chen et al. (2014a) and others showed that frying soybean oil improved the fatigue and low temperature properties of aged asphalt (Chen et al. 2014a; Chen et al. 2014b; Xinxin et al. 2018).

Triglycerides can also be obtained from microalgae which are not used for human consumption and are, therefore, very attractive for bitumen recycling. Indeed, some researchers have started looking in more detail into the mechanistic effects of bio-oils on bitumen properties such as morphology and the rejuvenation mechanisms (Hung et al. 2017; Pahlavan et al. 2019).

Aiming at understanding better the effect of the individual components of vegetables oils on bitumen properties, in the present study, bitumen-rejuvenator blends were prepared by using two free fatty acids, oleic acid and linoleic acid, and one triglyceride, triolein, as model rejuvenators. The main focus was to study the rheological properties of bitumen-rejuvenator blends after thermal aging (heating at 150 °C and 180 °C for 5 h). The thermal aging increased sufficiently the stiffness of bitumen and enhanced the differences between the blends. However, some blends were studied under unaged conditions for comparison purposes. The 5 and 10 wt% of rejuvenators used in the present study are in the concentration range studied by other authors (Yu et al. 2014; Zaumanis et al. 2014; Nahar et al. 2014; Zaumanis et al. 2015; Huang et al. 2015; Moghaddam and Baaj 2016; Cavalli et al. 2018).

Molecular compatibility between aged bitumen and rejuvenators and their potential by-products produced after aging is very important for preserving the properties of the recycled bitumen over time. Some studies have raised questions about the difference between softening and rejuvenation, questioning if the rejuvenators are working only as diluents of aged bitumen or if they are actually restoring the chemical composition of the original bitumen (Moghaddam and Baaj 2016; Karlsson and Isacsson 2006). Oleic acid, linoleic acid and triolein are not likely to be found in the original composition of bitumen. Therefore, the restoration of the original chemical composition of bitumen by the addition of these vegetable oil components is excluded. Nevertheless, molecular incompatibility resulting in phase separation of the blends was not visible under the conditions studied. Hence,

this basic study provides some guidance on the selection of the vegetable oil type to those looking for more sustainable alternatives for rejuvenators.

Experimental section

Materials

Different physical and chemical properties of the investigated straight run bitumen with penetration grades 160/220 and 10/20 are presented in Table 1. These grades were chosen since they mark the extreme cornerstones of practical application. Gel permeation chromatograms can be found in the Supporting Information, Figure S1. According to the European Standard EN1426, the penetration is expressed as 10 times the depth in millimeter that a standard needle under a load of 100 g will penetrate vertically into a bitumen sample at a temperature of 25 °C after 5 s. The softening point as per the European Standard EN 1427 is defined as the temperature at which the bitumen under standardized conditions attains a specific consistency that is characterized by a critical temperature where a standard steel ball creates a defined bitumen deformation.

Oleic acid (OA) 90 %, linoleic acid (LA) 60 – 74 % and triolein (Tri) ~ 65% were obtained from Sigma Aldrich and used without further purification. Their chemical structure is shown in Figure 1 and properties provided by the supplier and measured in this study, such as viscosity before (room temperature, RT) and after different thermal treatments (150 °C for 5 h and 180 °C for 5 h) are presented in Table 2.

As shown in Figure 1 the main difference in the molecular structure between oleic acid and linoleic acid is a second C=C bond in the latter. Triolein is composed of three oleic acid molecules connected covalently through ester bonds to a glycerol moiety. Therefore, the molecular weight of triolein is approximately three times higher than that of oleic acid and linoleic acid.

Linoleic acid and triolein with high purity, ≥ 99 %, purchased from Sigma Aldrich, produced similar results compared with lower purity rejuvenators (Supporting Information, Figure S2).

Sample preparation

Preparation of aged bitumen

To obtain a batch of aged bitumen that was subsequently blended with unaged rejuvenators, the original bitumen was aged as follows. 15 g of bitumen were placed in a metal pan of 12 cm diameter, heated and spread to cover its bottom and obtain films of around 2 mm thickness. The bitumen was then thermally aged (heated) under air by placing the metal pan in a ventilated oven at 150 °C for 5 h. The aged bitumen is designated as aged 150-5-1 and described in Table 3.

Preparation of aged rejuvenators

To age the rejuvenators, 0.5 to 1 mL of oleic acid, linoleic acid and triolein were placed in 5 mL open glass vials exposed to air and heated at 150 and 180 °C for 5 h in the ventilated oven. The designation of the aged rejuvenators is described in Table 3.

Preparation of blends of unaged, aged bitumen and rejuvenators

The blends of unaged bitumen and rejuvenators were prepared by weighing 5 g of bitumen and 0.25 g or 0.5 g of rejuvenator in the same container and then heated at 130 °C in a ventilated oven for 10 min to enhance blending of the low viscosity liquid. After constant and vigorously stirring the blend by hand using a metal spatula for 2 min, the bitumen+rejuvenator blend was placed back in the oven for another 10 min. Thereafter, vigorous stirring with the spatula for another 2 min was repeated and finally the blend was left to cool down at room temperature.

The preparation of blends of aged bitumen as described earlier was performed with unaged rejuvenators according to the same procedure as followed by unaged bitumen and rejuvenators. The only difference in the process was the use of aged bitumen instead of unaged. The designation of the unaged and aged bitumen and blends is described in Table 3.

Preparation of aged bitumen-rejuvenator blends

Bitumen-rejuvenator blends were prepared as follows. Unaged bitumen and unaged rejuvenators blends prepared as described above were placed in silicone molds and heated at 150 and 180 °C for 5 h to produce thermally aged samples. The temperatures of 150 and 180 °C were selected because they are within the range of temperatures used for manufacturing hot mixtures of asphalt concrete. Original bitumen alone was aged with the same procedure for direct comparison. Thermally aged blends and bitumen by this procedure are designated as aged 150-5-2 and aged 180-5-2 and described in Table 3.

Note that the aging procedure of the samples did not follow the conventional procedures of bitumen aging with rolling thin film oven test (RTFOT) or pressure aging vessel (PAV). However, the change in the properties (e.g. stiffness and oxidation) of bitumen and blends achieved by the thermal treatment used was enough to show the different effect of the rejuvenators on aged bitumen. The procedure used produced sufficiently homogeneous blends confirmed by the unchanged aspect during the period of several months and the reproducibility of the results. The procedure is acceptable for very small blends produced with cycles of high temperature and controlled time of stirring; however, to avoid any inconsistency by hand-mixing, in particular for larger samples, a mechanical stirrer is recommended.

For the rheological measurements, 0.2 – 0.25 g of bitumen or bitumen-rejuvenator blends were placed in silicone disc molds with 8 mm diameter and 2 mm height and heated in a ventilated oven at 110 °C for 20 min. This

procedure was used to produce a similar thermal history in all samples before the rheological measurements. The measurements were performed within 48 h after the thermal treatment.

For the attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy measurements, a small amount of bitumen and bitumen-rejuvenator blends was spread on glass slides over an area of approximately $3 \times 3 \text{ mm}^2$, and heated in a ventilated oven at 110°C for 20 min as well as at 150°C and 180°C for 5 h. Thereafter, the samples were removed from the oven and left to cool down to room temperature ($21.5 \pm 1.5^\circ\text{C}$). The measurements were performed within 48 h after the thermal treatment.

Measurement methods

The rheological properties of bitumen and bitumen-rejuvenator blends were determined using a dynamic shear rheometer (DSR) Physica MCR 301 from Anton Paar. The oscillatory and rotational measurements were performed by using the plate-plate geometry with 8 mm diameter and a gap of 1 mm. The oscillatory measurements were performed within the linear viscoelastic region at constant strain amplitude of 0.05 % and in 10°C temperature steps in the temperature range 30 to 0°C . Between each temperature step a (thermal) equilibration time of 10 min was allowed. The frequency range was $20 - 0.1 \text{ Hz}$ and the measurements were performed from the higher to the lowest frequency. The following equations define the rheological parameters measured or calculated.

$$G' = \frac{\sigma_0}{\varepsilon_0} \cos \delta \quad (1)$$

$$G'' = \frac{\sigma_0}{\varepsilon_0} \sin \delta \quad (2)$$

$$\frac{G''}{G'} = \tan \delta \quad (3)$$

where, σ_0 and ε_0 are the stress and strain amplitudes of harmonic sinusoidal oscillation; and δ is the phase angle characterizing the time shift between stress and strain oscillations; the so-called storage modulus G' and loss modulus G'' are the real (elastic) and imaginary (viscous) parts of the complex shear modulus $|G^*|$ which is defined as the ratio of stress and strain amplitudes:

$$|G^*| = \frac{\sigma_0}{\varepsilon_0} = \sqrt{G'^2 + G''^2} \quad (4)$$

The obtained curves enabled the construction of the “master curve” of $|G^*|$ through the time-temperature superposition principle and using the Williams–Landel–Ferry (WLF) equation (Moghaddam and Baaj 2016; Ferry 1980). The master curve was determined for the reference temperature of 20°C .

The rotational measurements were used to measure the shear viscosity of the rejuvenators using a shear rate in the range of $100 - 1000 \text{ s}^{-1}$.

ATR-FTIR measurements were performed at room temperature (20 – 23 °C) in a Tensor 27 spectrometer from Bruker in the ATR mode using a diamond crystal. The bitumen samples were placed with the bitumen surface against the diamond crystal. For the rejuvenators, one drop was placed on the ATR crystal. The spectra were collected in the 4000 – 600 cm^{-1} wavenumber range with a resolution of 4 cm^{-1} , each spectrum representing an accumulation of 32 spectra.

Thermogravimetric analysis (TGA) was performed by using a TG 209F1 standard/P thermogravimetric analyzer. Approximately 7 mg of the sample were heated from 30 to 700 °C at the heating rate of 20 °C/min under O_2 atmosphere.

Results and discussion

Figure 2 shows the complex shear modulus $|G^*|$ and the phase angle δ for bitumen-rejuvenator blends aged thermally at 150 °C for 5 h (aged 150-5-2).

Thermal aging of bitumen 160/220 increased the value of $|G^*|$ by a factor of 4 for 10^{-1} Hz and 2 for 10^3 Hz relatively to the unaged state. For bitumen 10/20, $|G^*|$ increased by a factor of 1.5 for 10^{-1} Hz and kept a similar value for 10^3 Hz relatively to the unaged state.

For 5 wt% of the three rejuvenators only triolein kept the complex shear modulus below that of aged bitumen 160/220 over the whole frequency range i.e., 36 % lower at 10^{-1} Hz and 33 % lower at 10^3 Hz.

As shown in Figure 2 a) at lower frequencies the blend with linoleic acid had higher $|G^*|$ than aged bitumen while $|G^*|$ for the blend with 5 wt% of oleic acid was 5 % lower than that of aged bitumen.

10 wt% of triolein in the blend had a greater effect than 10 wt% of oleic and linoleic acid for both bitumen types as shown in Figure 2 a) and c). For the blends with bitumen 10/20 and 10 wt% of oleic acid $|G^*|$ decreased 80 % at 10^{-1} Hz and 53 % at 10^3 Hz. However, $|G^*|$ decreased 91 % at 10^{-1} Hz and 71 % at 10^3 Hz for the blend with triolein.

Interestingly, the aged bitumen-rejuvenator blends with 5 wt% of rejuvenators presented a lower δ i.e. a more elastic behavior than aged bitumen (Figure 2b), and for 10 wt% rejuvenator, the δ values became similar to those of aged bitumen. A similar trend was also observed for the blends of unaged bitumen and unaged rejuvenators in particular for the case of bitumen 160/220 (Supporting Information, Figure S3). On the contrary, unaged oleic acid added to aged bitumen was able to decrease $|G^*|$ to a greater extent than triolein (Supporting Information, Figure S4). Moreover, a more viscous behavior i.e. increase in δ was observed. Addition of 10 wt% of the three aged rejuvenators to unaged bitumen produced a similar decrease in $|G^*|$ (Supporting Information, Figure S5). Interestingly, adding unaged rejuvenators to unaged bitumen 10/20 seems to result in dilution or softening i.e. the viscous response prevails. A possible explanation for these observations is that unaged rejuvenators act as

diluents or dispersing agents when added to aged bitumen leading to both decrease in stiffness and increase in the viscous response. This phenomenon could be explained by the fact that unaged bitumen 10/20 contains a different chemical composition compared to unaged bitumen 160/220. Bitumen is a mixture of many different molecules classified into four major chemical groups referred to as asphaltenes, resins, saturates and aromatics. In terms of molecular weight, asphaltenes and resins have the highest molecular weight. Elementally bitumen is mostly carbon and hydrogen and smaller amounts of sulphur, nitrogen and oxygen. Table 1 shows that bitumen 10/20 contains more oxygen and higher molecular weight than bitumen 160/220. This is expected because harder bitumen is typically concentrated in asphaltenes and resins. Harder bitumen can be produced by high temperatures as it is also demonstrated in this study. Therefore, unaged rejuvenators may work as diluents or dispersing agents of asphaltenes when added to harder or aged bitumen resulting in softening. In such a case, the dilution or dispersing efficiency would be more pronounced for the smaller rejuvenators due to their chemical structure and/or the higher number of molecules compared to triolein.

On the other hand, the molecular interactions in unaged bitumen and unaged rejuvenator blends and the molecular interactions developed in aged (at 150 °C) bitumen-rejuvenator blends seem to favor an elastic response over the viscous as compared with aged bitumen.

Corroborating the complexity of the blends, upon thermal aging of bitumen-rejuvenator at even a higher temperature (180 °C), the end effect showed a decrease in $|G^*|$ and increase in δ compared with aged bitumen as shown in Figure 3.

The thermal aging at 180 °C for 5 h increased the value of $|G^*|$ of bitumen 160/220 by a factor of 28 at 10^{-1} Hz and 3 at 10^3 Hz relatively to the unaged bitumen.

Similar trends were observed as for the thermal aging of bitumen-rejuvenator blends at 150 °C and 5 h in terms of $|G^*|$. For 5 wt% of rejuvenators, only triolein kept the rejuvenating effect in the blend and for 10 wt% triolein showed a greater rejuvenating effect than oleic and linoleic acids after thermal aging (Figure 3a). For example, as compared with aged bitumen, for the blend with 5 wt% triolein, $|G^*|$ decreased 72 % at 10^{-1} Hz and 49 % at 10^3 Hz. However, for the blend with 5 wt% linoleic acid, $|G^*|$ increased 1.1 times at 10^{-1} Hz and did not change for the blend with oleic acid. For the mixture with 5 wt% of oleic and linoleic acids, $|G^*|$ at 10^3 Hz decreased 6 % and 2 %, respectively. For the blend with triolein, 10 wt% of the rejuvenator produced a reduction of 96 – 77 % of $|G^*|$ in the range of 10^{-1} to 10^3 Hz. On the other hand, the decrease was of 60 – 30 % for the blend with 10 wt% of oleic acid.

In order to understand the molecular transformations in the bitumen-rejuvenator blends upon thermal aging ATR-FTIR measurements were conducted. First the rejuvenators alone were examined. After thermal aging, no

decrease in the volume of the rejuvenators sample was observed. However, there was a clear change in color for some of the rejuvenators. The change in color is an indicator of changes in chemical composition. Moreover, the sample of linoleic acid aged at 180 °C for 5 h looked like a paste at the top. Additionally, as shown in Table 2 the viscosity of the rejuvenators increased upon thermal treatment. It is well-known that vegetable oils undergo degradation at high temperatures due to chemical changes such as hydrolysis, oxidation, cyclization and polymerization reactions. During such processes, degradation products such as aldehydes, ketones, esters, alcohols, alkenes, alkanes, aromatic hydrocarbons and/or short chain carboxylic acids may form.

Figure 4 shows ATR-FTIR spectra for unaged and aged oleic acid, linoleic acid and triolein with close ups in specific regions of interest. In the Supporting Information (Table T1) band locations in the spectra of oleic acid, linoleic acid and triolein for the different functional groups and assignments of the various modes of vibration are reported (Weigel and Stephan 2017; Feng et al. 2016). Table 4 shows the mathematical area (the algebraic sum of trapezoids) for different bands including those depicted in Figure 4b), c) and d), calculated using the indicated integration limits and straight line-baseline ends. Figure 4a) shows the color of the rejuvenator samples before and after thermal aging.

It is well-known that in nonpolar or weakly polar solvents oleic and linoleic acids occur in a dimeric form at room temperature. This was also seen here by the intense band at 1708 cm^{-1} (Figure 4c) for the carbonyl group ($\text{C}=\text{O}$), characteristic of the dimer form of oleic acid formed due to hydrogen bonding. However, with the increase in temperature, dimers may change (gradually) into the monomer form (Noskov et al. 1980). The carbonyl group of the monomer appears at approximately around 1745 cm^{-1} (Figure 4c). This change is generally accompanied by the change in the OH absorption band at 2672 cm^{-1} (OH from dimeric COOH) which happens to a lesser degree here as shown in Table 4. However, the band around 1745 cm^{-1} falls in the region of the $\text{C}=\text{O}$ stretching vibration for esters (1750-1735 cm^{-1}) and aldehydes (1740-1720 cm^{-1}) and increased for the thermal aging (Last et al. 2009). This means that the fatty acids (or their fragments) have oxidized as a result of aging.

Other evidences of degradation were the change occurring for the $\text{C}=\text{C}$ stretching vibration mode at 1655 cm^{-1} (Figure 4d) and for the $=\text{CH}$ *cis* stretching vibration mode at 3006 and 3009 cm^{-1} (Figure 4b) (Christy et al. 2009; Kamal-Eldin et al. 2003). Both areas decreased (Table 4). Further evidences of significant changes in the spectra were observed, such as the decrease in the absorbance of the band at 1412 and 1378 cm^{-1} (Figure 4e) (Last et al. 2009).

The changes observed in the triolein ATR-FTIR spectrum due to thermal aging were not as significant as for the free fatty acid (Table 4). Therefore, less molecular changes, e.g., degradation and oxidation were detected in the case of triolein. Kamal-Eldin et al. (2003) have shown that temperatures above 140 °C do not produce losses of

triolein due to degradation which could be consistent with what is observed here. However, above 180 °C triglycerides can undergo oxidation and form aldehydes, aldehyde acids, alcohols and hydrocarbons (Christy et al. 2009). The degradation of the oils can actually result in a very complex mixture of components which may not be visible in great detail with infrared spectroscopy. Due to the degradation of polyunsaturated oils at high temperatures, oleic and saturated fatty acids are used more in cooking and frying at the expense of polyunsaturated acids such as linoleic acid (Kamal-Eldin et al. 2003). In case waste cooking, oils are used as bitumen rejuvenators this information should be considered (Li et al. 2020a; Li et al. 2020b).

ATR-FTIR spectroscopy measurements were also performed on the bitumen-rejuvenator blends in order to gain further insight into possible discrepancies at the molecular level between blends containing the different rejuvenators. Figure 5 shows ATR-FTIR spectra for the unaged and aged bitumen-rejuvenator blends aged for 150 °C for 5 h containing 5 and 10 wt% of rejuvenators. The infrared band assignments for bitumen can be found in the Supporting Information (Table T2).

Comparing Figure 5a) and b) with c) and d) show the disappearance of the carbonyl stretching vibration at 1708 cm^{-1} of oleic acid and the increase of the carbonyl bond stretching vibration of bitumen at 1698 cm^{-1} with the thermal aging due to oxidation. The disappearance of the carbonyl stretching vibration at 1708 cm^{-1} also occurred for linoleic acid (not shown here). This happened without the increase of the band at 1740 cm^{-1} in the case of the fatty acids alone (Figure 4c). This phenomenon could be due to coordination of the carboxylic group of the free fatty acids with components of bitumen. The spectrum of triolein remained identical to the unaged blend, indicating that the triolein rejuvenated bitumen was less susceptible to aging. The same effects were observed for the blends with bitumen 10/20 (not shown) and for the aged blends at 180 °C for 5 h.

The increase of the carbonyl band was used as indicator of oxidation. The oxidation of the bitumen-rejuvenator blends containing oleic acid and linoleic acid after thermal aging at 150 °C and 180 °C for 5 h was semi-quantified by calculating the mathematical area (the algebraic sum of trapezoids) of the carbonyl band $A_{C=O}$ for bitumen, using the integration limits 1730 and 1670 cm^{-1} for unaged bitumen and 1750 and 1640 cm^{-1} for the aged bitumen and bitumen-rejuvenator blends and straight line-baseline ends. The $A_{C=O}$ is shown in Table 5 together with the carbonyl index $I_{C=O}$. $I_{C=O}$ is the normalization of $A_{C=O}$ by the area under the bands at 1457 and 1375 cm^{-1} which is practically unaffected upon thermal aging and oxidative effects. The integration limits used for the calculation of the area under the bands at 1457 cm^{-1} were 1490 and 1394 cm^{-1} , and under the band at 1375 cm^{-1} were 1394 and 1350 cm^{-1} . For triolein, the calculation of the areas using this method was not possible due to the overlapping of the carbonyl bands of triolein and bitumen. However, it is observed that the blends containing triolein also oxidized as indicated by the appearance of the carbonyl stretching vibration band.

Thermal aging increased the area of the carbonyl stretching vibration band of bitumen. This means that the thermal aging led to the oxidation of bitumen and that higher temperature increased the oxidation state. Additionally, the oxidation seems to be slightly higher for the aged blends containing linoleic acid as compared to oleic acid for both thermal aging procedures. This could originate from the contributions of oxidized species resulting from the aging of the linoleic acid.

Additional information about the change in the molecular properties of aged rejuvenators and aged bitumen-rejuvenator blends was obtained with TGA measurements and is shown in Figure 6.

Figure 6a) shows that the thermal aging produced lower weight losses for the same temperature in the temperature range 300 to 500 °C for aged oleic acid as compared with unaged oleic acid. On the contrary thermal aging resulted in larger weight losses for the same temperature in the temperature range between 300 and 400 °C in aged triolein as compared with the unaged triolein. These observations could be directly related to the formation of larger molecules upon thermal aging in the oleic acid case and the formation of smaller molecules in the case of aged triolein. This could be in favor of the decrease of stiffness as smaller molecules are formed.

Figure 6b) shows the TGA curves for unaged and aged bitumen 160/220 and selected bitumen-rejuvenator blends. Upon thermal aging, the TGA curve of aged bitumen shows a clear extra step between 350 and 400 °C. A similar step is observed in the TGA curve of unaged bitumen 10/20 (Lee et al. 2016). The same happens for the aged bitumen-rejuvenator blends. This change is most likely correlated with oxidation and the resulting increase of the molecular weight of bitumen upon thermal aging. No significant difference between the aged blend with oleic acid and triolein could be seen.

The results seem to indicate that the higher stability of triolein and/or eventually its transformation into smaller molecules at high temperatures, observed in the TGA measurements, can contribute to lower stiffness and higher viscous behavior of the bitumen-triolein blends.

Conclusions

This study provides basic knowledge to determine the effect of the type of rejuvenator and aging on their performance. To this end, it was shown that the chemical nature of the components of vegetable oils (rejuvenators) has a strong impact on the rheological properties of bitumen-rejuvenator blends. Although the three different components, oleic acid, linoleic acid and triolein, at the two dosages 5 and 10 wt%, are able to reduce the stiffness of aged bitumen and contribute to enhance the viscous behavior of the final blend, the scenario is different when the bitumen-rejuvenator blends are aged under high temperature. After thermal aging of bitumen-rejuvenator blends with 5 wt% of oleic acid and linoleic acid had similar or higher complex shear

modulus and lower viscous response compared to aged bitumen. Only the bitumen-rejuvenator mixtures with 5 wt% triglyceride presented considerably lower values of the complex shear modulus compared with aged bitumen. For the highest aging temperature (180 °C) used not only the stiffness decreased with the presence of triolein, but also the viscous response increased when compared with aged bitumen. For the highest dosage, the softening effect of triolein was higher in comparison to the other two rejuvenators. This demonstrates that the chemical changes happening to the triglyceride at high temperatures contribute to lower stiffness and higher viscous behavior of the bitumen-triolein blends. Therefore, vegetable oils with high content of triglycerides, possibly with lower unsaturation, would be recommended if long-term performance of recycled bitumen is desired. As for future research, it would be of great interest to study the ageing of blends of aged bitumen and aged rejuvenators aiming at understanding the rejuvenation effect of waste cooking oils for sustainability reasons.

Acknowledgments

The authors thank the Swiss National Science Foundation (200020_152980/1) for financial support, Sivottha Hean for performing the GPC measurements, and Beatrice Fischer for performing the TGA measurements.

Data Availability Statement

- Some or all data, models, or code that support the findings of this study are available from the corresponding author upon reasonable request.
- All data, models, and code generated or used during the study appear in the submitted article.

References

- Asli, H., Ahmadiania, E., Zargar, M., & Karim, M. R. 2012. Investigation on physical properties of waste cooking oil-Rejuvenated bitumen binder. *Construction and Building Materials*, 37, 398-405.
- Bockish, M. 1998. Composition, structure, physical data, and chemical reactions of fats and oils, their derivatives, and their associates. *Fats and oils handbook*, 53-120.
- Cavalli, M. C., Zaumanis, M., Mazza, E., Partl, M. N., & Poulikakos, L. D. 2018. Effect of ageing on the mechanical and chemical properties of binder from RAP treated with bio-based rejuvenators. *Composites Part B: Engineering*, 141, 174-181.
- Chen, M., Leng, B., Wu, S., & Sang, Y. 2014b. Physical, chemical and rheological properties of waste edible vegetable oil rejuvenated asphalt binders. *Construction and Building materials*, 66, 286-298.

368 Chen, M., Xiao, F., Putman, B., Leng, B., & Wu, S. 2014a. High temperature properties of rejuvenating
 369 recovered binder with rejuvenator, waste cooking and cotton seed oils. *Construction and Building*
 370 *Materials*, 59, 10-16.

371 Christy, A. A., Xu, Z., & Harrington, P. D. B. 2009. Thermal degradation and isomerisation kinetics of triolein
 372 studied by infrared spectrometry and GC–MS combined with chemometrics. *Chemistry and physics of*
 373 *lipids*, 158(1), 22-31.

374 Feng, Z. G., Wang, S. J., Bian, H. J., Guo, Q. L., & Li, X. J. 2016. FTIR and rheology analysis of aging on
 375 different ultraviolet absorber modified bitumens. *Construction and Building Materials*, 115, 48-53.

376 Ferry, J. D. 1980. *Viscoelastic properties of polymers*. John Wiley & Sons.

377 Huang, S. C., Qin, Q., Grimes, W. R., Pauli, A. T., & Glaser, R. 2015. Influence of rejuvenators on the physical
 378 properties of RAP binders. *Journal of Testing and Evaluation*, 43(3), 594-603.

379 Hugener, M., Partl, M. N., & Morant, M. 2014. Cold asphalt recycling with 100% reclaimed asphalt pavement
 380 and vegetable oil-based rejuvenators. *Road materials and pavement design*, 15(2), 239-258.

381 Hung, A. M., Mousavi, M., Pahlavan, F., & Fini, E. H. 2017. Intermolecular interactions of isolated bio-oil
 382 compounds and their effect on bitumen interfaces. *ACS Sustainable Chemistry & Engineering*, 5(9),
 383 7920-7931.

384 Kamal- Eldin, A., Velasco, J., & Dobarganes, C. 2003. Oxidation of mixtures of triolein and trilinolein at
 385 elevated temperatures. *European journal of lipid science and technology*, 105(3- 4), 165-170.

386 Karlsson, R., & Isacson, U. 2006. Material-related aspects of asphalt recycling—state-of-the-art. *Journal of*
 387 *materials in civil Engineering*, 18(1), 81-92.

388 Last, D. J., Nájera, J. J., Percival, C. J., & Horn, A. B. 2009. A comparison of infrared spectroscopic methods for
 389 the study of heterogeneous reactions occurring on atmospheric aerosol proxies. *Physical Chemistry*
 390 *Chemical Physics*, 11(37), 8214-8225.

391 Lee, J. B., Dos Santos, S., & Antonini, C. 2016. Water touch-and-bounce from a soft viscoelastic substrate:
 392 Wetting, dewetting, and rebound on bitumen. *Langmuir*, 32(32), 8245-8254.

393 Lesueur, D. 2009. The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of
 394 bitumen modification. *Advances in colloid and interface science*, 145(1-2), 42-82.

395 Li, C., Han, X., Gong, J., Su, W., Xi, Z., Zhang, J., Wang, Q. and Xie, H. 2020a. Impact of waste cooking oil on
 396 the viscosity, microstructure and mechanical performance of warm-mix epoxy asphalt
 397 binder. *Construction and Building Materials*, 251, p.118994.

398 Li, R., Bahadori, A., Xin, J., Zhang, K., Muhunthan, B., & Zhang, J. 2020b. Characteristics of bioepoxy based
 399 on waste cooking oil and lignin and its effects on asphalt binder. *Construction and Building*
 400 *Materials*, 251, 118926.

401 Marsac, P.; Pierard, N.; Porot, L.; Van den bergh, W.; Grenfell, J.; Mouillet, V.; Pouget, S.; Besamusca, J.;
 402 Farcas, F.; Gabet, T.; Hugener, M. 2014. Potential and limits of FTIR methods for reclaimed asphalt
 403 characterisation. *Materials and Structures*, 47 (8), 1273-1286.

404 Mattson, F. H., & Volpenhein, R. A. 1963. The specific distribution of unsaturated fatty acids in the triglycerides
 405 of plants. *Journal of lipid research*, 4(4), 392-396.

406 Moghaddam, T. B., & Baaj, H. 2016. The use of rejuvenating agents in production of recycled hot mix asphalt:
 407 A systematic review. *Construction and Building Materials*, 114, 805-816.

408 Nahar, S.N., Qiu, J., Schmets, A.J.M., Schlangen, E., Shirazi, M., Van de Ven, M.F.C., Schitter, G. and Scarpas,
 409 A., 2014. Turning back time: rheological and microstructural assessment of rejuvenated
 410 bitumen. *Transportation Research Record*, 2444(1), pp.52-62.

411 Noskov, A. M.; Komlev, A. M.; Vershinin, E. A. 1980. IR spectroscopic study of the decomposition of dimers
 412 of oleic and elaidic acids. Plenum Publishing Corporation, 1531-1534.

413 Pahlavan F, Samieadel A, Deng S, Fini E. 2019. Exploiting Synergistic Effects of Intermolecular Interactions to
 414 Synthesize Hybrid Rejuvenators to Revitalize Aged Asphalt. *ACS Sustainable Chemistry &*
 415 *Engineering.*, 14;7(18):15514-25.

416 Petersen, J. C., & Glaser, R. 2011. Asphalt oxidation mechanisms and the role of oxidation products on age
 417 hardening revisited. *Road Materials and Pavement Design*, 12(4), 795-819.

418 Poulikakos, L. D., dos Santos, S., Bueno, M., Kuentzel, S., Hugener, M., & Partl, M. N. 2014. Influence of short
 419 and long term aging on chemical, microstructural and macro-mechanical properties of recycled asphalt
 420 mixtures. *Construction and Building Materials*, 51, 414-423.

421 Weigel, S., & Stephan, D. (2017). The prediction of bitumen properties based on FTIR and multivariate analysis
 422 methods. *Fuel*, 208, 655-661.

423 Xinxin, C., Xuejuan, C., Boming, T., Yuanyuan, W., & Xiaolong, L. 2018. Investigation on possibility of waste
 424 vegetable oil rejuvenating aged asphalt. *Applied Sciences*, 8(5), 765.

425 Yu, X., Zaumanis, M., Dos Santos, S., & Poulikakos, L. D. 2014. Rheological, microscopic, and chemical
 426 characterization of the rejuvenating effect on asphalt binders. *Fuel*, 135, 162-171.

427 Zaumanis, M., Mallick, R. B., & Frank, R. 2015. Evaluation of different recycling agents for restoring aged
 428 asphalt binder and performance of 100% recycled asphalt. *Materials and Structures*, 48(8), 2475-2488.

Zaumanis, M., Mallick, R. B., Poulikakos, L., & Frank, R. 2014. Influence of six rejuvenators on the performance properties of Reclaimed Asphalt Pavement (RAP) binder and 100% recycled asphalt mixtures. *Construction and Building Materials*, 71, 538-550.

List of Figure Captions:

Figure 1 Chemical structure of the rejuvenators: a) oleic acid (OA), b) linoleic acid (LA) and c) triolein (Tri).

Figure 2 $|G^*|$ as a function of frequency (a, c) and as a function of the phase angle δ (b, d) for the bitumen-rejuvenator blends aged at 150 °C for 5 h with bitumen 160/220 (a, b) and bitumen 10/20 (c, d). OA: oleic acid, LA: linoleic acid and Tri: triolein. The curves show the average values of two measurements with a difference of less than 10 %.

Figure 3 a) $|G^*|$ as a function of frequency and b) as a function of the phase angle δ for the bitumen-rejuvenator blends aged at 180 °C for 5 h with bitumen 160/220. The curves show the average values of two measurements with a difference of less than 10 %.

Figure 4 a) ATR-FTIR spectra of unaged oleic acid (OA), linoleic acid (LA) and triolein (Tri) and after thermal aging at 150 and 180 °C for 5 h. The spectra were shifted vertically by the value indicated on the right side for clarity. The change in color for the rejuvenators upon thermal aging is also shown on the right side. Curves in b), c), d) and e) are specific parts of the spectra showing changes in absorbance of A, B, C and D bands (no vertical shifting).

Figure 5 Left: ATR-FTIR spectra of a) unaged blends of bitumen 160/220, oleic acid (OA) and triolein (Tri) and c) aged blends at 150 °C for 5 h. Right: close up on the area corresponding to carbonyl stretching vibration band for b) unaged blends and d) aged blends at 150 °C for 5 h. The spectra were shifted vertically by the value indicated on the right side of a) and c) for clarity.

Figure 6 Thermogravimetric analysis (TGA) curves obtained under O₂ for a) unaged and aged oleic acid (OA) and triolein (Tri), at 180 °C for 5 h and b) unaged bitumen 160/220, aged 180-5-2 160/220, and unaged and aged at 180 °C for 5 h bitumen-rejuvenator blends.

List of Table Captions:

Table 1 Properties of the investigated bitumen types. Elemental analysis from previous study (Lee et al. 2016).

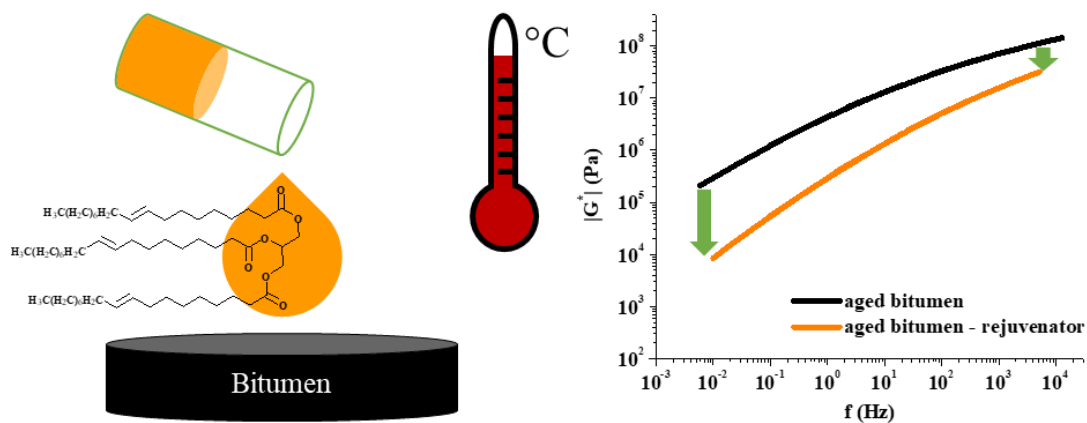
Table 2 Properties of the rejuvenators: Oleic acid (OA) 90 %, linoleic acid (LA) 60 – 74 % and triolein (Tri) ~ 65%. RT: room temperature.

Table 3 Designation of the different samples. X = Oleic acid (OA), linoleic acid (LA) or triolein (Tri).

458 **Table 4** Area under different bands for oleic acid (OA), linoleic (LA) acid and triolein (Tri) for the different
 459 thermal treatments.

460 **Table 5** Area of carbonyl stretching vibration ($A_{C=O}$) and carbonyl index $I_{C=O}$ for the unaged and aged bitumen
 461 and aged bitumen-rejuvenator (oleic acid and linoleic acid) blends. OA: oleic acid, LA: linoleic acid.

462 **Graphic Abstract**



463

Table 1 Properties of the investigated bitumen types. Elemental analysis from previous study (Lee et al. 2016).

	Penetration (× 0.1 mm)	Softening point (°C)	Carbon (wt%)	Hydrogen (wt%)	Nitrogen (wt%)	Sulphur (wt%)	Oxygen (wt%)	Molecular weight (g/mol)
Bitumen 160/220	184	39.8	83.75	10.21	1.00	4.80	0.22	780
Bitumen 10/20	18	69.2	84.31	10.00	0.82	4.14	0.72	1330

2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

21 **Table 2** Properties of the rejuvenators: Oleic acid (OA) 90 %, linoleic acid (LA) 60 – 74 % and triolein (Tri) ~
 22 65%. RT: room temperature

	Freezing point (°C)	Boiling point (°C)	Molecular weight (g/mol)	Density (g/cm³)	Viscosity RT/150 °C-5 h/180 °C-5 h (mPa s)
OA - Oleic acid	13 – 14	194 – 195 at 1.6 hPa	282.46	0.87	29/36/69
LA - Linoleic acid	5	229 – 230 at 21 hPa	280.45	0.90	22/49/67
Tri - Triolein	-12 – -5	235 – 240 at 24 hPa	885.43	0.91	83/99/113

23
 24
 25
 26
 27
 28
 29
 30
 31
 32
 33
 34
 35
 36
 37
 38
 39
 40
 41
 42
 43
 44
 45

46 **Table 3** Designation of the different samples. X = Oleic acid (OA), linoleic acid (LA) or triolein (Tri).

Sample designation	Description
unaged 160/220	Unaged bitumen 160/220
unaged 160/220 + X	Unaged bitumen 160/220 blended with rejuvenator
unaged 10/20	Unaged bitumen 10/20
unaged 10/20 + X	Unaged bitumen 10/20 blended with rejuvenator
aged 150-5-1 160/220	Bitumen 160/220 aged at 150 °C for 5 h
aged 150-5-1 160/220 + X	Aged bitumen 160/220 blended with rejuvenator
aged 150-5-2 160/220	Bitumen 160/220 aged at 150 °C for 5 h (in silicone mold)
aged 180-5-2 160/220	Bitumen 160/220 aged at 180 °C for 5 h (in silicone mold)
aged 150-5-2 160/220 - X	Blend of bitumen 160/220 and rejuvenator aged at 150 °C for 5 h
aged 180-5-2 160/220 - X	Blend of bitumen 160/220 and rejuvenator aged at 180 °C for 5 h
aged 150-5-2 10/20	Bitumen 10/20 aged at 150 °C for 5 h (in silicone mold)
aged 150-5-2 10/20 - X	Blend of bitumen 10/20 and rejuvenator aged at 150 °C for 5 h
X 150 °C	Rejuvenator aged at 150 °C for 5 h
X 180 °C	Rejuvenator aged at 180 °C for 5 h

47

48

49

50

51

52

53

54

55

56

57

58

59

60

61 **Table 4** Area under different bands for oleic acid (OA), linoleic (LA) acid and triolein (Tri) for the different
62 thermal treatments

Rejuvenator	Bands (cm ⁻¹)	Functional group and mode of vibration	Integration limits (cm ⁻¹)	Area		
				20 °C	150 °C-5 h	180 °C-5 h
LA	3009	=CH <i>cis</i> stretching LA	3035 – 2990	0.38	0.30	0.22
OA	3006	=CH <i>cis</i> stretching OA	3035 – 2990	0.21	0.18	0.14
Tri	3006	=CH <i>cis</i> stretching Tri	3035 – 2990	0.17	0.15	0.13
OA	2672	OH (from dimeric COOH) stretching OA	2706 – 2620	0.20	0.17	0.15
LA	2672	OH (from dimeric COOH) stretching LA	2706 – 2620	0.19	0.17	0.15
Tri	2672	OH (from dimeric COOH) stretching OA, LA	2706 – 2620	0.05	0.04	0.05
OA	1740 + 1708	C=O stretching OA	1770 – 1670	7.74	7.70	7.88
LA	1740 + 1708	C=O stretching LA	1770 – 1670	7.89	7.84	8.25
Tri	1740	C=O ester Fermi resonance Tri	1770 – 1670	5.62	5.69	5.90
Tri	1655	C=C stretching Tri	1665 – 1637	0.026	0.024	0.015

63

64

65

66

67

68

69

70

71

72

73

74

75

76 **Table 5** Area of carbonyl stretching vibration ($A_{C=O}$) and carbonyl index $I_{C=O}$ for the unaged and aged bitumen
77 and aged bitumen-rejuvenator (oleic acid and linoleic acid) blends. OA: oleic acid, LA: linoleic acid.

Bitumen/Bitumen-rejuvenator	$A_{C=O}$	$I_{C=O} = A_{C=O} / (A_{1457} + A_{1375})$
unaged 160/220	0.003	0.0007
aged 150-5-2 160/220	0.67	0.14
aged 150-5-2 160/220 - OA 5 wt%	0.49	0.11
aged 150-5-2 160/220 - LA 5 wt%	0.67	0.15
aged 150-5-2 160/220 - OA 10 wt%	0.37	0.08
aged 180-5-2 160/220	0.90	0.20
aged 180-5-2 160/220 - OA 5 wt%	0.89	0.20
aged 180-5-2 160/220 - LA 5 wt%	1.01	0.23
unaged 10/20	0.039	0.008
aged 150-5-2 10/20	0.54	0.12
aged 150-5-2 10/20 - OA 5 wt%	0.39	0.085
aged 150-5-2 10/20 - LA 5 wt%	0.76	0.17
aged 150-5-2 10/20 - OA 10 wt%	0.63	0.14

78

Figure 2

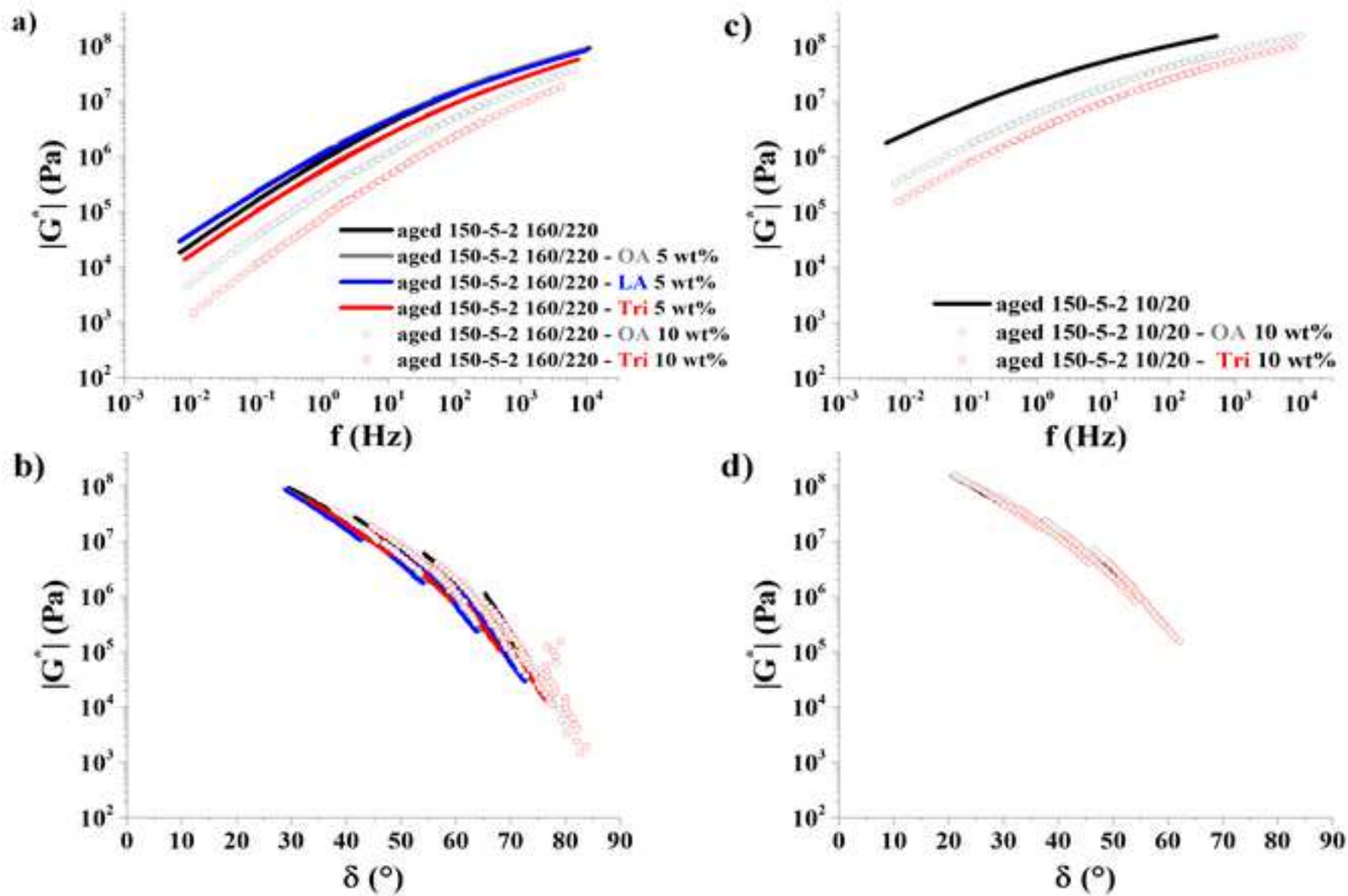
[Click here to access/download;Figure;Figure 2.tif](#)

Figure 3

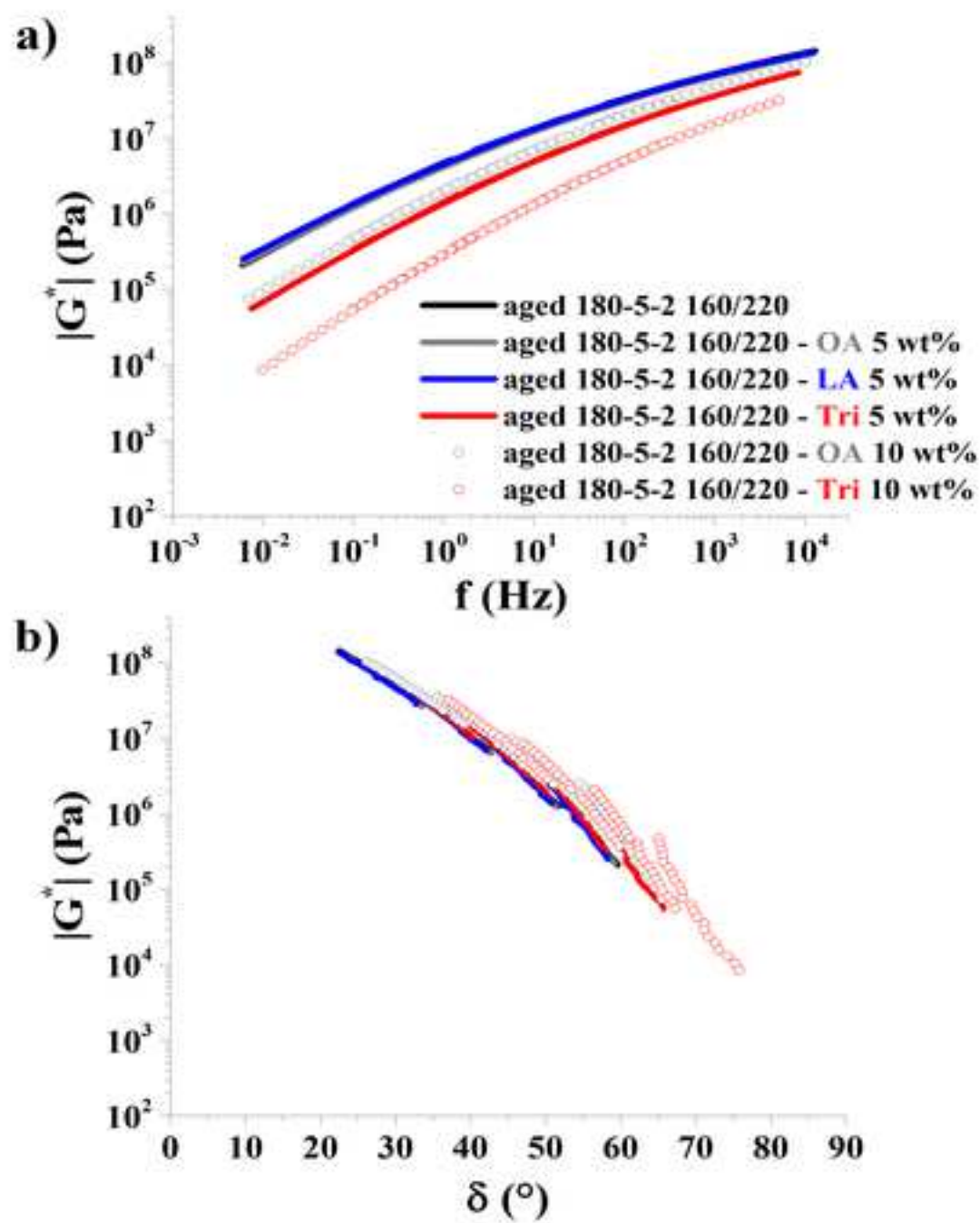


Figure 4

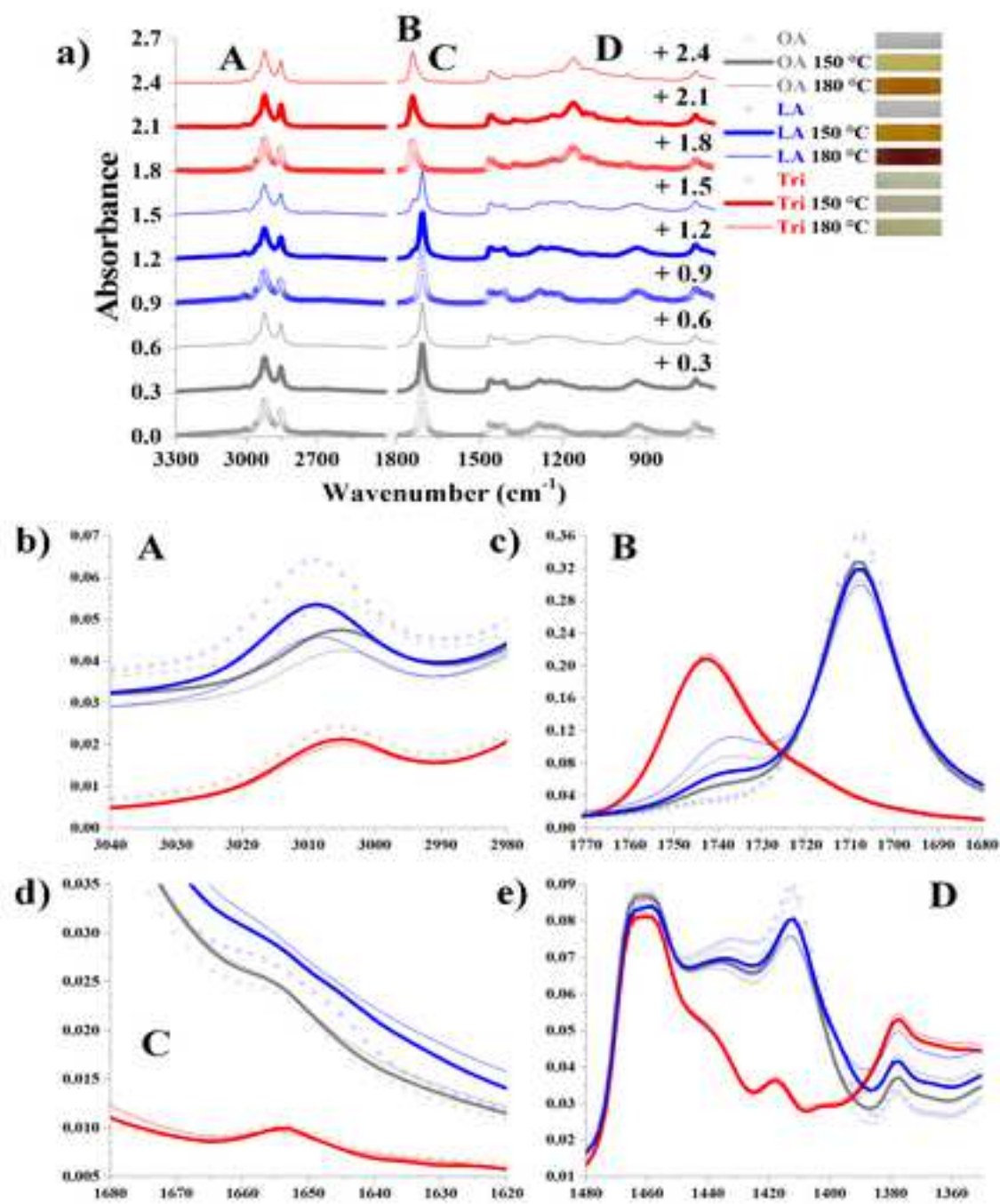


Figure 5

[Click here to access/download;Figure;Figure 5.tif](#)