SYNTHESIS, CHARACTERIZATION, AND FUNCTIONALIZATION OF RENEWABLE VEGETABLE OIL MODIFIED WITH MALEIC ANHYDRIDE

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ABSTRACT

Nowadays, the continuous increase in the production sustainability of the leather industry should be considered an ordinary challenge. The implementation of green processes and the utilization of natural or recycled resources, maintaining high performance of the final products, are innovative methods to reduce the economic, social, and environmental impacts.

This research aims to provide a series of eco-sustainable functionalized materials, based on maleic anhydride and natural oils, as efficient and environmentally friendly alternatives to petrochemical substances. The originality of the study consists of the evaluation of a new class of bio-based adducts including grape, hempseed, and linseed oils. These natural sources were selected for their marginal economic and social impact, and their structural properties, such as the high content of unsaturated fatty acids, as advantageous sites to functionalize triglyceride molecules.

Moreover, the standard thermal synthesis was compared to the microwave irradiation process, as an alternative technique providing reduced energy consumption, minimized pollution, rapidity, and simplicity in processing.

The structural analyses and the grafted effectiveness of maleic anhydride on vegetable oils were supported by Fourier Transformed Infrared spectroscopy and Nuclear Magnetic Resonance. Acid-base titration provided information on the performance of anhydride functionalization.

The practical objective of the present research was to provide new bio-based, sustainable, and eco- friendly materials, such as functionalized vegetable oils, as efficient alternatives for leather industry applications including fat liquoring, impermeabilization, and re-tanning.

Keywords: Sustainability, Renewability; Vegetable oils

1. Introduction

The increasing and alarming abuse of fossil fuels in industrial processes, leads to negative impacts both in the environmental, economic, and social spheres, highlighting the importance to shift to renewable materials and energy resources. As with almost all human activities, tanneries are responsible for severe environmental pollution and potential health hazards, hence, the improvement of the environmental and social assessment of these processes is fundamental. Among the renewable alternatives for modern industries, vegetable oils may represent suitable materials as natural and sustainable products due to their availability, biodegradability, inherent safety, and affordable cost. Vegetable oils are hydrophobic materials, their structure mainly consists of a glyceryl moiety connected with an ester bond to three fatty acid chains which vary in terms of length and number of double bonds (Iodine number). Oleic (1), linolenic (2), and linolenic are among the most common fatty acids in vegetable oils. Stearic or palmitic fatty acids may also be present in vegetable oils, they have saturated bonds on the chain. In previous studies, natural oils, and animal or vegetable fats have been employed to produce fat-liquor agents. However, natural oils are low soluble in water, thus, they must be chemically modified to obtain higher solubility and water emulsion (WEN et al., 2022). Alkenyl succinic anhydrides are materials frequently

used in the hydrophobic sizing of paper, epoxy resin setting agents, corrosion inhibitors, leather−finishing agents, additives in fuels, lubricants, paints, and thickeners in foods, juices, and puddings. They consist of five−membered anhydrides with branched iso−alkenyl chains (JOAQUÍN, 2003). Usually, they are prepared to start from unrenewable petroleum olefins and maleic anhydride (MA). Maleic anhydride represents a sustainable material, easily, economically, and environmentally friendly produced that is approximately 72% more profitable and 38% more eco-efficient than the benzene process (MANGILI et al., 2019). Natural oils may represent a renewable alternative to petroleum olefin. There are mainly three different ways to achieve efficient synthesis. The first is the Alder−Ene mechanism: MA, containing multiple bonds, is called enophile, and the unsaturated fatty acid chain containing allylic hydrogen is known as 'Ene'. The ene-reaction consists of the formation of a new σ-bond, due to the migration of the double bond of the fatty acid chain (ene) and a hydrogen shift. The new carbon−carbon single bond created results in the loss of the double bond on the anhydride ring. The second and third routes are essentially radical additions. In the first one, the double bond of the carbon chain of the fatty acid is employed to incorporate the succinic anhydride into the vegetable oil structure. In the second the radical addition is activated by the deprotonation of hydrogen lying between the two alkenes groups. The result is the bond of the maleic anhydride into the fatty acid structure without any consumption of double bonds (ALARCON et al., 2020b).

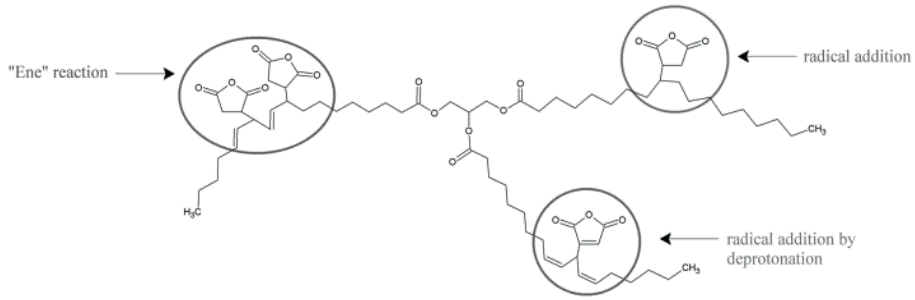


Figure 1: Possible mechanism of the reaction

Linolenic and linoleic polyunsaturated fatty acids, with their higher number of unsaturated bonds, are expected to be more reactive concerning monounsaturated fatty acids, and oleic fatty acids. Vegetable oils including hemp seed, linseed and grapeseed are rich in polyunsaturated carbon chains, these seem to have favourable properties for efficient synthesis. Furthermore, the use of vegetable oils with a high amount of double bonds performs stronger binding on the leather substrate. High iodine value can be found in fish oils, but they usually give leather an unpleasant smell, on the other hand, catching marine fish has slightly decreased in the last decades (ZARŁOK et al., 2014). This highlights the importance of the use of alternative vegetable oils for benefits from an environmental and economical point of view. In previous literature, different vegetable oils have been used to synthesize functionalized macromonomers with maleic anhydride including soybean, cottonseed, and castor oils (ALARCON et al., 2017; BOGA et al., 2019a; ECHEVERRI et al., 2012).

In the tannery industry, fat liquors are surface-active agents traditionally based on oil-water emulsions. Oils are not soluble in water; thus, they are usually sulphated or sulfonated, stabilized with a hydrophilic functionalization (KAMELY, 2022). Moreover, for specific sectors, like footwear, and clothing for wet and cold conditions, the water resistance of leather is an essential property. When leather absorbs a high amount of water it can lose its insulation quality against both water, heat, and cold temperature. Moreover, these clothes and footwear should assure high water vapour permeability and reversible water uptake to remove perspiration from human bodies. In general, when water spreads on the surface of leather, it penetrates the inner layers, wetting the fibre networks. The leather results are soaked by water molecules due to the interaction between the polar functional groups of collagen polypeptide. Due to the previous tannery process, also other agents, such as salts, dye molecules etc. can be involved in this mechanism. There are different approaches applied to produce waterproof leather. One is to hold the leather with an impermeable polymer like a foil of synthetic material on the leather surface bonded as an

adhesive. This method reduces the permeability of the leather. The second one consists of the impregnation of the leather with fat or oily substance. This is a traditional method, but it produces a heavy product, and it prevents the air and vapour permeability of the leather. Finally, a smarter method, concerning the previously mentioned, consists of the use of the so-called open waterproofing (JANKAUSKAITE et al., 2012). The waterproof agent, with its hydrophobic layer, can coat the leather fibres. Water vapour can penetrate the fibre network; but the water droplets, with higher surface tension, cannot spread over the hydrophobic surface and wet the inner part of the leather. The creation of bonds between the fibres and the agent is required, thus the amphiphilic character of the waterproof material is essential. Our research studies the possibility to modify vegetable oils with maleic anhydride to produce waterproof agents with a sustainable and green character. Nowadays, the most performing waterproofing agents are based on silicon, mineral oil, and fluorinated materials that are typically non- renewable and neither eco-friendly. In our research, we approached a new synthetic route based on renewable resources (maleic anhydride and vegetable oils) for tannery processes, including waterproof leather. The production of hydrophobic leather, as part of the total leather process, must be performed in an aqueous environment. Thus, the chemicals used must be dissolved in water, which means they must contain hydrophilic groups compatible with water. For this reason, maleic anhydride (MA) can be used to functionalize the material. MA, bonded to the fatty acid (FA) chains, reacts with sodium hydroxide, its ring opens, and the two carboxyl groups enhance the solubility of the overall material. In this way, the MA-based oil-water emulsion can penetrate the skin, covering the leather fibres, and react with the main functional group of collagens like NH^{+}. Moreover, opened anhydride rings can create complexes with chromium molecules, present in the leather inner layer from the tannery process, stabilizing the overall structure. The relatively long hydrophobic chains of the triglyceride represent the hydrophobic side of the molecule. A simple scheme of the structure of the molecule and the wet-blue tanner leather are shown in **Figure 2.**

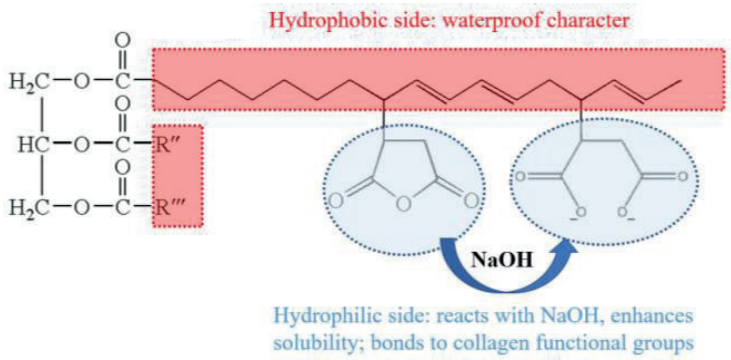


Figure 2: Waterproof agent structure

In this work, hemp seed, linseed, and grapeseed oils have been used as precursors for waterproof agents. The suitability of the synthetic approach was evaluated according to adequate characterization: FTIR, NMR, and titration analyses. Final fat-liquor formulations have been performed according to standard procedure. For the first time, the effect of new natural oils-based fat-liquors on impermeabilization properties has been examined, beyond the usual mechanical and organoleptic characteristics. Higher sustainability in the fat-liquoring preparation was also proposed in terms of energy saving. For what concerns the preparation of alkenyl succinic anhydrides, the high activation energy (E > 80 kJ/mol) requires high temperatures (> 200°C) and a long reaction time (2-8 hours) (ALARCON et al., 2017;
STEFANOIU et al., 2008). Microwaves have been used as an alternative, eco-friendly and economical technique. Lower reaction time and lower energy consumption are among the advantage of this technology. Moreover, it has been recognized that microwave radiation can be more than conventional heating due to its direct effect on reactants with a faster and more homogeneous control of reaction temperature. The advantages are explained by two main effects: first a thermal effect, the temperature rises faster than the conventional method of heating, which decreases reaction time and energy consumption., secondly a non−thermal effect, due to the electrostatic polar interaction between chemicals and magnetic field, due to the increase of kinetic efficiency, and decrease of activation energy (ALARCON et al., 2020b). In the current work, microwave-based reactions have been performed as potential approaches for more sustainable tannery processes.

2. Experimental

2.1 Material and Methods

Vegetable oils were supplied by a generic supermarket: soybean, grapeseed (GO), linseed (LO), and hempseed (HO). Maleic anhydride (MA, 99%) was supplied by Sigma Aldrich.

2.2 Standard Synthesis

Standard synthesis (STD) followed traditional procedures with some modifications [1,2]. A three-neck round flask with a capacity of 2000 mL was placed on a heating mantle. A typical batch experiment is performed with the different molar ratios between maleic anhydride and oil. The reaction was kept for 2h at a temperature of 200°C reached with a rate of about 5°C/min.

2.3 Microwave Synthesis

Microwave-based syntheses (MW) were performed on a Monowave 200 (Anton Paar). The volumes were kept on a laboratory scale (10 mL) and proportionally to the STR synthesis (molecular ratio MA:oil 0.5). The reactions were kept for 45 minutes at a temperature of 230°C reached with a rate of 5°C/min

2.4 Characterization

Perkin−Elmer Spectrum 100 FTIR spectrophotometer was employed for FTIR using NaCl plates or KBr pellet for respectively viscous solids (wavenumber range of 4000−500 cm^{-1}). A 600 MHz Bruker Avance spectrometer equipped with a cryoprobe was employed for NMR analyses, and samples were dissolved in $CDCl_3$ (7.26 ppm). The content of maleic anhydride bonded succinic was quantified by acid titration.

2.5 Fat-liquoring procedure and waterproof tests

The 4 supplied wet-blue hides weigh 100g., all the amounts are referring to the dry weight of the hides. Before the waterproof treatment, the wet-blue hides were washed with water, stabilized with chromium, and fixed with sodium formate. The pH was adjusted with bicarbonate. The MA-grafted vegetable oil adduct was dissolved in NaOH (1.5%) to partially open the anhydride rings and solubilize the material. After the fatliquoring treatment, chromium was added to the mixture to create complexes with unreacted anionic functional groups and fixed with formic acid. A scheme of the procedure is reported in **Table 1** A dynamic waterproof leather testing machine (Bally penetrometer 5125) was used to measure the performance.

Table 1: Scheme of the overall fatliquoring treatment

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Process:		**retanning**	
Input	**Amount (%)**	**Temperature (°C)**	**Time (min)**
water	200	25	60
Cr 23/33	3		
Process:		**Pre-fat liquoring (until pH=5)**	
Sodium formate	1	25	30
Sodium bicarbonate	0.8	25	45
Process:		**Drain and washing**	
Process:		**Fat liquoring**	
WP agent	10	50	
water	100	60	
Process		**Fixing (till pH=3.5)**	
Formic acid	1	25	30
water	150		
Process		**Complex COOH Esterification**	
Cr 23/33	2	25	30
Process		**Fixing**	
Formic acid	1	25	30

3. Results and Discussion

3.1 Characterisation of raw material

3.1.1 FTIR

The characteristic FTIR spectra of the raw vegetable oils, soybean, grape, hempseed, and linseed are presented in **Figure 3**. All spectra show similar features. The peak at 1744 cm^{-1} corresponds to the C=O of the triglyceride and was used as a reference. The methylene groups (-CH_2-) can be assigned to the following peaks: 1465, 3011, and 1654 cm^{-1} (GUILLÉN; CABO, 1997). At 720, 1654, and 3011 cm^{-1} we assigned the disubstituted olefins signals of the long acyl chain (WANG et al., 2020). From the spectra, we can assume that most of the double bonds are cis configurations. As expected, the linseed and the hempseed oils contain higher unsaturated bonds than the grapeseed oils, the lower amount belongs to the soybean oils, that is mainly composed of a one-unsaturated fatty acid, oleic acid.

3.1.2 NMR

The chemical shifts of ^1H were assigned; the results agreed with those found in the literature for raw vegetable oils (STEFANOIU et al., 2008). The assignment is resumed in **Table 2**. An estimation of the percentage of the principal fatty acids in the different oils has been made according to traditional methods (ZHANG et al., 2018), results are shown in **Table 3**.

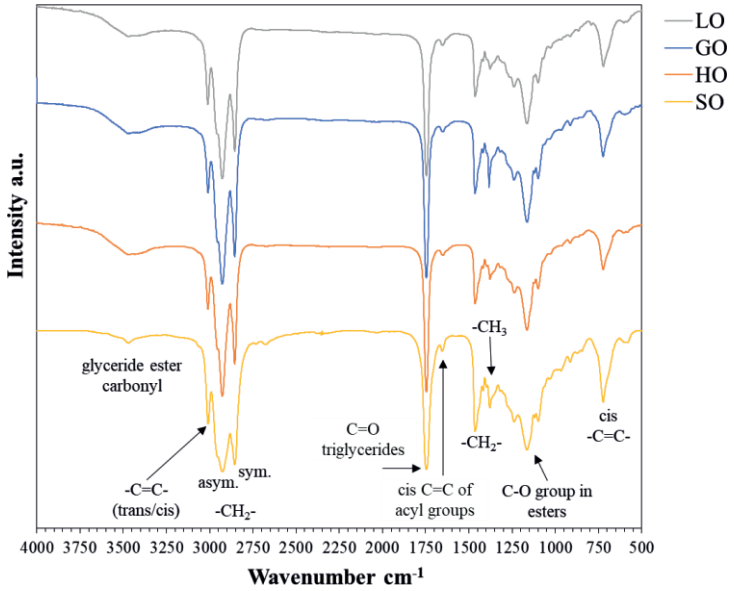


Figure 3: FTIR spectra of the raw materials LO, GO, HO, and SO

^{1}H-NMR ppm	assignation
0.91, 0.99	–C**H**3 positions A
1.26-1.38	–C**H**2– positions C
1.62	–O–C(=O)–CH2–C**H**2– positions F
2.07	(=C–C**H**2–) position G
2.32	–O–C(=O)–C**H**2–CH2– positions E
2.78	–C=C–C**H**2–C=C– positions M
4.1-4.3	glyceryl group (triglyceride) position I.
5.28	glyceryl group (triglyceride) position H.
5.38	alkene hydrogen [–C**H**=C**H**–] position L

Table 2: Assignment of 1H-NMR of Linseed oil

	GO	HO	LO	SO
Linolenic %	1.96	18.03	51.21	5.24
Linoleic %	66.66	57.37	20.48	21.26
Oleic %	20.35	14.35	20.14	29.72
Saturated FA	11.03	10.25	8.17	43.78

Table 3:Percentage of fatty acids per type of oil

3.2 Characterisation of maleinizated vegetable oils

3.2.1 FTIR

The reaction was monitored with FTIR, as a function of temperature and time, to understand its proceeding. At 100°C an evident increase of the peaks at 699 cm^{-1}, 842 cm^{-1}, 888 cm^{-1}, 1780 cm^{-1}, and 1851 cm^{-1} correspond to MA. The bands corresponding to 1783 cm^{-1} and 1744 cm^{-1} can be attributed to symmetric and asymmetric stretching of C=O in the anhydride ring (ALARCON et al., 2020a).
As shown in **Figure 4**, by raising the temperature from 150 to 200°C and enhancing the reaction time the consumption of unreacted MA was recorded according to the decreasing of the peaks at 699 cm-1 and 842 cm-1. On the other side, the peak corresponding to the succinic anhydride (SA) bonded to the triglyceride chain was recorded according to the increase of the peaks at 1863 cm^{-1}, it was also associated with the carbonyl group of the anhydride as an overtone of the band at 918 cm^{-1} (LAURE; CARLOS; ELISABETH, 2005). These results were found in agreement with other reports on maleinization processes (AIGBODION et al., 2003; CARBONELL-VERDU et al., 2017). Moreover, the increase in time reaction also produced an important change in colour from a pale yellow, characteristics of the common vegetable oils to brownish proceeding, (**Figure 4**) similar results were reported in previous studies (GUILLÉN; CABO, 1997).

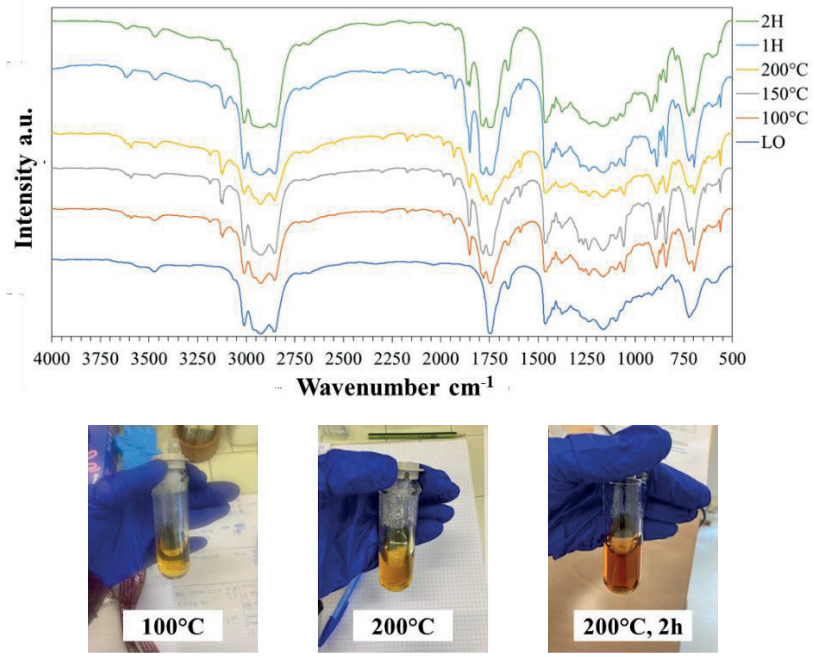


Figure 4: FTIR of LOMA, photo of LOMA at different synthetic temperatures

The effects of different synthetic parameters were monitored with FTIR. The molar ratio between oil and maleic anhydride was enhanced from 1:1 (LOMA) to 1:2 (LOMA+). As shown in **Figure 5A**, the increase of maleic anhydride during the synthetic procedure was reflected as the relative increase of the peaks corresponding to the grafted anhydride (1863 cm^{-1}). Moreover, the standard procedure was performed under a nitrogen atmosphere (LOMA N2). The effect of the controlled condition was a decrease of peaks corresponding to OH bands (3200-3700 cm^{-1}). This reflects lower oxidation of oils due to the absence of oxygen molecules; the advantage of the

controlled atmosphere consists of a decrease in thermal degradation and a suitable colour effect, which can be advantages according to the industrial application of the synthesized material (VOLLI; PURKAIT, 2014). The FTIR spectra for microwave-based synthesis (MW LOMA) were found to be similar to the standard (LOMA), this leads to the conclusion that non-thermal effects can be neglected in the modified synthetic procedure and good dispersion of the microwave radiations inside the reactor (**Figure 5B**). Similar results were already recorded in the literature (ALARCON et al., 2020b).

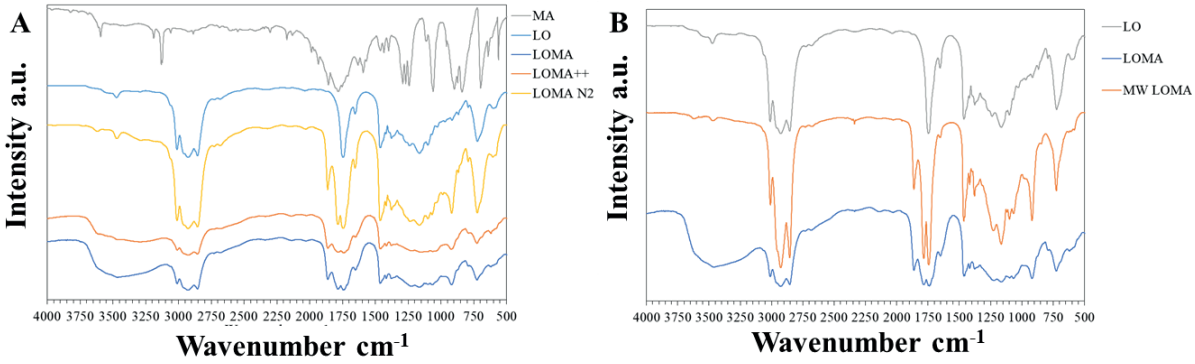


Figure 5: FTIR of MA, LO, LOMA, LOMA, LOMA N2, MW LOMA

The increasing concern on environmental issues due to the abuse and consequent depletion of petroleum makes it essential the use alternative natural sources in industrial applications to create new, greener, and more sustainable opportunities. As an alternative, we considered the employ of different raw vegetable oil for the synthesis of maleic-based material for tannery applications. We further consider soybean (SO), hempseed (HO), and grapeseed oil (GO), beyond the already discussed linseed oil (LO). All synthesis has been performed with similar methods, the FTIR spectra are shown in **Figure 6**. According to the results, all the vegetable oils considered are suitable raw materials for the synthetic procedure performed. However, considering the same time and temperature synthetic parameters, different maleic anhydride consumption rates have been recorded. In order from the faster to the slower HO>GO>SO, this has been concluded from the relative decrease of the peak at 699 cm^{-1}, a characteristic band of unreacted maleic anhydride. Hempseed oil was found to consume faster maleic anhydride for the higher unsaturated degree. Indeed, hempseed oil, like linseed oil, has a high content of linolenic fatty acid that contains three double bonds. Beyond the different synthetic efficiency, different raw vegetable oils have a different impact on the final colour of the material, this is an important consideration for the future application in industrial processes.

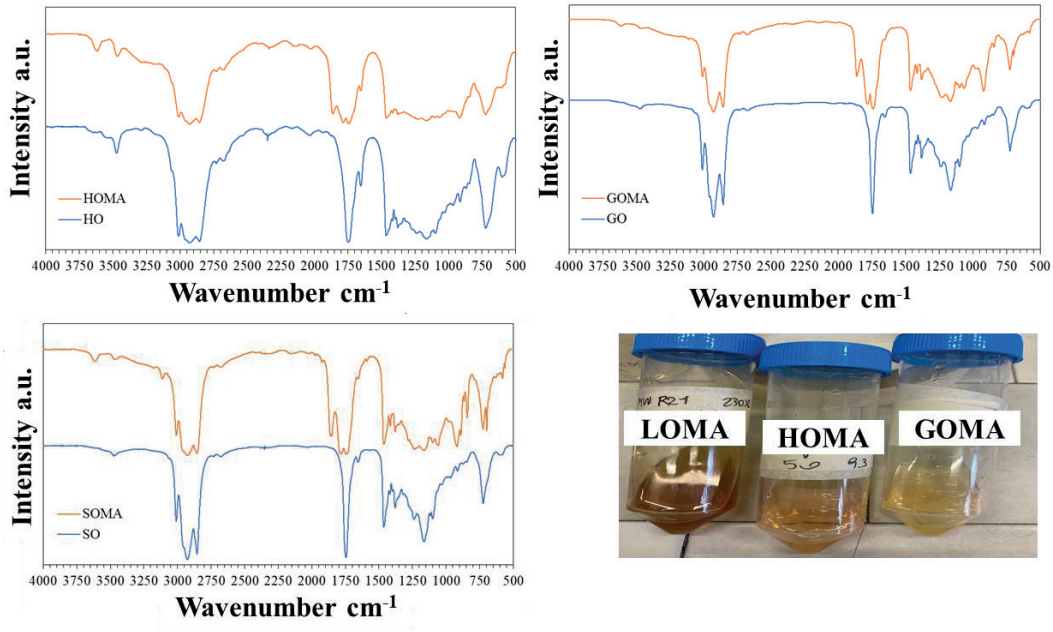


Figure 6: FTIR raw oils and maleinized oils, photo of the prepared materials

3.2.2 NMR

The $^{1}H-NMR$ spectra of the raw linseed oil, LOMA, and LOMA+ were recorded. The dominant peaks are represented by the fatty acid chain bonds of the raw vegetable oils. The peak at 7.25 is the characteristic peak of the solvent (chloroform). The singlet at 7.05 ppm is assigned to the hydrogen of unreacted maleic anhydride. As shown in **Figure 7A** the unreacted maleic anhydride peak decrease with the time proceeding of the reaction, as expected because it reacts with the double bonds of the fatty acid chains. The zoom of the previous spectra is presented. The assignment of peaks at 3.2 and 2.9 ppm confirmed the bonding between the MA and the vegetable oil, according to FTIR analyses. The $^{13}C-NMR$ spectrum of LOMA has been recorded and the assignation is shown in **Figure 7B**. The appearance of new signals corresponds to the grafted anhydride on the fatty acid acrylic chain. In particular, the carbon of the grafted anhydride (–$\mathbf{C}H_2$–) in position A is assigned to the region between 45 and 50 ppm (BOGA et al., 2019b). Signals appearing around 180 ppm correspond to the carbonyl carbon of MA grafted on the vegetable oil (MAGANU et al., [s.d.]).

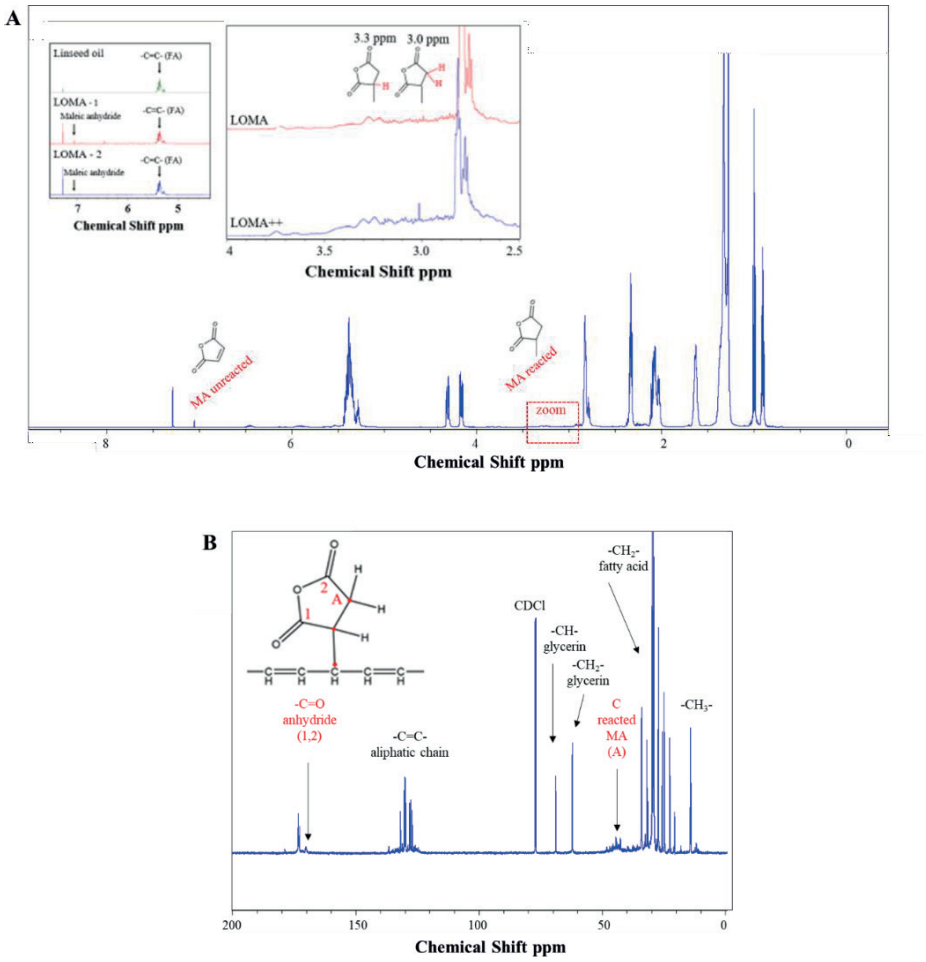


Figure 7: A) 1H-NMR of LO, LOMA-1 (200°C), LOMA-2 (200°C-2h), LOMA (1:1 mw%), LOMA+ (2:1 mw%); B) 13C-NMR of LOMA

3.2.3 Titration

The amount of grafted anhydride was quantified by acid titration. The quantity of anhydride was calculated per gram of adduct following the literature methods with some modifications (ZOVI et al., 2011). For standard syntheses, the grams of MA per gram of waterproof agent (WP agent) were respectively 0.16, 0.15, and 0.12 for GOMA, HOMA, and LOMA. In microwave-assisted syntheses higher amount of grafted MA was recorded, 0.18 for GOMA, 0.2 for HOMA, and 0.24 for LOMA. The results show higher efficiency in microwave-assisted reaction, probably due to the controlled atmosphere applied during the synthetic method.

3.3 Hydrophobicity test by determination of water-resistance of flexible leather: repeated linear compression (penetrometer) (ISO 5403- 1:2011)

A traditional bally waterproofness tester was used on the treated samples to test leather dynamic water penetration resistance ability. A test piece is formed into the shape of a trough and flexed while partially immersed in water. The time taken for water to penetrate through the test piece is measured. The method also allows for the percentage mass of the water absorbed and the mass of the water transmitted through
the test piece to be determined. The penetration of water was measured on samples flexing the materials under a certain speed (cycles/min) to simulate the water resistance and the daily work. The order from the more efficient waterproof agent to the lower one is LOMA>SOMA>GOMA>LOMA+. From the previous results, we conclude that the enhancement of maleic anhydride in the MA-grafted vegetable oil does not correspond to increasing waterproof ability, when an optimum value has been reached the molecules tend to assume a hydrophilic character. Moreover, we assume that the more efficient waterproof ability of the LOMA, MA-grafted to linseed oil, can be associated with a higher percentage of poly-unsaturated fatty acid (linolenic, linoleic). The presence of a higher amount of double bonds leads to the higher viscosity of the waterproof agent, which results in a greater capacity to penetrate through the fibres and bonds to collagen.

4. Conclusions

The global waterproof footwear market is in continuous growth due to the importance of human comfort in outdoors products. Non-eco-friendly and non-renewable waterproof agents and processes are commonly applied in tannery industries to achieve the required performance of leather products. The growing consciousness of the necessity of sustainable industries implies the necessity of enhancement of the scientific and technological value of products and processes, giving particular attention to the environment and ecosystems. Recently, the use of bio-based materials, such as vegetable oils, and the application of renewable technologies, such as microwave energy, have represented new possibilities also in the leather market. The vegetable oils, rich in unsaturated fatty acids, were employed in the present research due to their low economic value, non-toxicity, and availability. Microwave technology was applied to decrease the energetic demand of the synthetic process of waterproof agents. Different vegetable oils were used and compared. MA-grafted linseed oil (LOMA) was found to be a more efficient waterproof agent than the others. Microwave technology was found to be suitable for decreasing reaction time and energy consumption during the synthetic procedure. Further studies are needed to improve the waterproofing ability of the materials and to optimize the synthetic route on an industrial scale. However, the present results represent a valuable alternative to the current waterproof agents. The potential of vegetable oils applications and the implementation of microwave heating are worth investigating and investing in future research efforts.

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Note