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Autooxidized Polyunsaturated Oils/Oily Acids: Post-it Applications and Reactions with Fe(III) and Adhesion Properties

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Summary: Soybean oil, sesame oil, linoleic acid and linolenic acid were epoxidized, peroxidized and hydroperoxidized via autooxidation under air oxygen and sunlight at room temperature to obtain novel post-it materials. Polymeric soybean oil peroxide and sesame oil peroxide were containing soluble part of 60%(w/w) together with crosslinked part of 40%(w/w) while polymeric linoleic and polymeric linolenic acids were completely soluble. The autooxidized soluble products with Mn varying between 800 and 3100 Daltons were used as post-it adhesive. The highest adhesion was observed in the case of polymeric soybean oil (3.0 Newton), while adhesion of commercial epoxidized soybean oil, polymeric linoleic and polymeric linolenic acid were 0.8, 0.5 and 0.5 Newton, respectively. Reactions of the autooxidized soluble products with $Fe(NO_3)_3$. $4H_2O$ in the presence of ethanol, glycerol and diethyleneglycol gave the hydroxy functionalized products with the same M_n values and indicating no adhesive properties. When the commercial epoxidized soybean oil was reacted with $Fe(NO_3)_3$. $4H_2O$ in the presence of the alcohols, Mn of the hydroxy functionalized polymeric oil was found to be unchanged. ^{1}H NMR, FT-IR, SEM and GPC techniques were used in the characterization of the products obtained.

Keywords: autooxidation; biopolymer; hydroxyl functionalization; modification; polyunsaturated oil/oily acids; post-it adhesive

Introduction

Due to the accelerating depletion of petroleum reserves and increasing cost of petroleum, the replacement of petroleum with renewable resources, such as plant and animal products has gained importance.[1] Natural oils and fats are considered to be the most important class of renewable resources for the production of biodegradable polymers. Vegetable oils are an economical and environmentally friendly alternative to petroleum for biodegradable polymer synthesis in several ways. The first is direct polymerization of the oils; for example, a copolymerization with divinyl benzene and styrene leading to thermoset copolymers, or by polymerization of vinyl, maleic anhydride, glycidyl ether, and norbornyl derivatives of the oil.[2–8] The second is the production of poly(3-hydroxyalkanoates) (PHAs) as an energy reserve material for some microorganisms by using plant and fish oils.[9–13] The third is the polymerization of the unsaturated oils via autooxidation including peroxidation and epoxidation. [14–17] Recent studies focused on grafting reactions of monomers on naturally occurring peroxidized polymeric drying oils/oily acids. [18–20] In this manner, soybean oil, which is one of the polyunsaturated oils, can be modified by autooxidation, and then their peroxides, epoxides and perepoxides are formed for use as post-it materials and in the hydroxylation of the polymeric oils.

In this study efforts were focused on the diversification of the soluble polymeric

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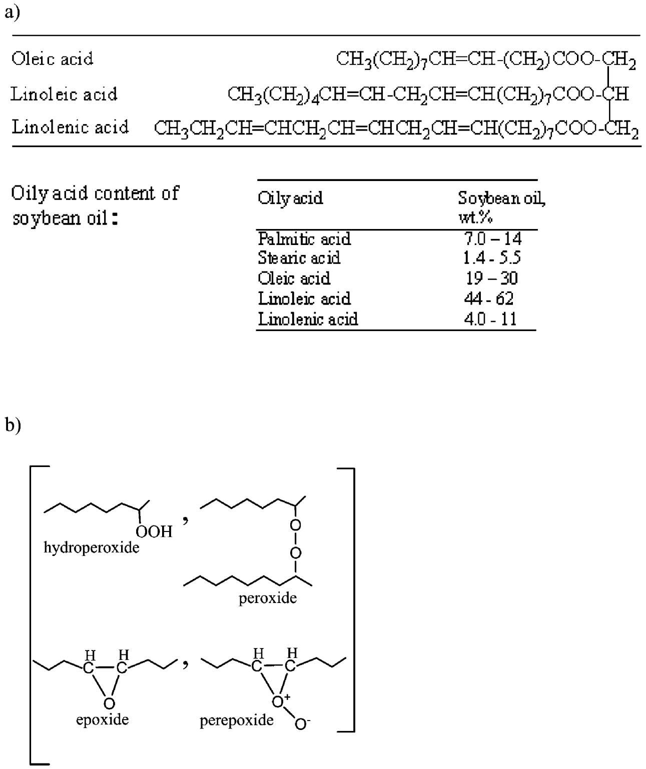


a)

Oleic acid $CH_3(CH_2)_7CH=CH\text{-}(CH_2)COO\text{-}CH_2$

Linoleic acid $CH_3(CH_2)_4CH=CH\text{-}CH_2CH=CH(CH_2)_7COO\text{-}CH$

Linolenic acid $CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COO\text{-}CH_2$

Oily acid content of soybean oil:

Oily acid	Soybean oil, wt.%
Palmitic acid	7.0 – 14
Stearic acid	1.4 - 5.5
Oleic acid	19 – 30
Linoleic acid	44 - 62
Linolenic acid	4.0 - 11

b)

Scheme 1.

Soybean oil composition and autooxidation products. a) Triglyceride structure for soybean oil (Mn 900 Daltons).[21] b) Formation of autooxidation products.

oils/oily acids for new application areas in industry and bioengineering. This work refers to post-it adhesive applications and hydroxy functionalization reactions of the autooxidized polymeric oils/oily acids.

Material and Methods

Materials

Soybean oil (Syb), sesame oil (Ssm), linoleic acid (Lina), linolenic acid (Lnlna) and commercial epoxidized soybean oil (Eps), and ethanol, EtOH, were obtained locally. Diethylene glycol, $Et(OH)_2$, and glycerol, $G(OH)_3$, and $Fe(NO_3)_3$ $4H_2O$ were supplied by Sigma-Aldrich (Germany).

Methods

^1H NMR spectra were recorded at Varian XL 200 in $CDCl_3$ with TMS as an internal standard. The IR analysis was performed on a Perkin-Elmer Pyris 1 FT-IR spectrometer using KBR disks or THF solution. The molecular weight of the polymeric samples was determined by gel permeation chromatography (GPC) (Knauer GmbH, Germany). Chloroform was used as the eluent at the flow rate of 1.0 $mL \cdot min^{-1}$. A calibration curve was generated with polystyrene standards. Scanning electron micrographs(SEM) were taken on a Jeol Feg-SEM JSM 6335F scanning electron microscope.

Autooxidation of Syb, Ssm, Lina and Lnlna

The oils/oily acids spread in a petri dish were auotoozidized in air at room temperature as previously described[20] For example, 5 g of soybean oil was spread out in a petri dish (ϕ 10 cm) and exposed to sunlight in the air at room temperature. After 2 months, a crosslinked film formed on the surface was stripped from the lower layer waxy-pale yellow polymeric oil soluble in organic solvent and was used through out this work. Characterization results: M_w: 5100, M_n: 3100 and peroxygen, %(w/w): 3.2. The soluble part: 60%(w/w), Crosslinked part: 40%(w/w).

Ring Opening of Epoxide with $Fe(NO_3)_3 \cdot 4H_2O$

In general, 1 g of autooxidized oil/oily acid, 2 mL of alcohol and 0.5 g of $Fe(NO_3)_3 \cdot 4H_2O$ was stirred for 2 days at room temperature. The crude mixture was dissolved in 20 mL of THF. The solution was filtered and poured into 200 mL of distilled water to precipitate the hydroxy functionalized polymeric oil. Then the product was dried under vacuum at room temperature. The pale yellow color of the substrate turned to dark reddish brown after the ring opening reaction.

Test of Adhesion Forces

In order to measure the adhesion forces of the autooxidized and hydroxy functionalized polymeric oils/oily acids prepared in this work, the device shown in Figure 1 was designed. For a typical measurement, the autooxidized soybean oil (Psyb) was smeared on the glass plates (2 cm × 1 cm) and then it was covered with the same size paper-like commercial pos-it. A dynamometer arm was stapled on the top of the covered paper. The adhesion values on the dynamometer were recorded at the moment the paper peeled-off the glass plate.

Results and Discussion

Soybean oil, sesame oil, linoleic acid and linolenic acid were epoxidized, peroxidized and hydroperoxidized via autooxidation under air oxygen and sunlight at room temperature. Polymeric soya oil peroxide (Psyb) and sesame oil peroxide (PSsm) contained a soluble part of 60%(w/w) together with a crosslinked part of 40%(w/w) while polymeric linoleic (Plina) and polymeric linolenic acids (Plnlna) were completely soluble. Molecular weight of the soluble polymeric oils/oily acids (M_n) were found to be between 950 and 2700 Daltons. Autooxidation process of the oils proceeds with the formation of epoxide, hydroperoxide and peroxide. At the beginning, polymerization of the oil leads to the soluble oligomers, then as polymerization progresses, a crosslinked polymeric oil film covers the surface. Soluble part of the polymeric oil is an oil oligomer which formed epoxide, hydroperoxide and peroxide linkages. When the autooxidation time increases, soluble part of the polymeric oils

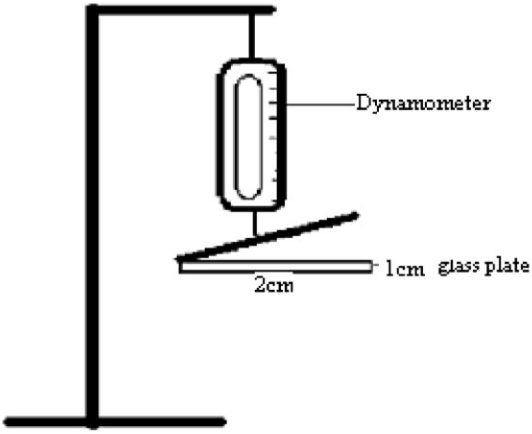


Figure 1.
Device for the adhesion force measurment.

transforms into the crosslinked polymeric oil film.

Characterization and Film Formation of the Hydroxy Functionalized Polymeric Oils/Oily Acids

Inspired by the synthesis of aerogel monoliths using cis-2,3-epoxybutane,[22] the polymeric oils/oily acids were reacted with Fe (III) salt in the presence of ethanol, diethylene glycol and glycerol to obtain hydroxy functionalized polymeric oils/oily acids. Fe(III) first opens the epoxide groups of the autooxidized oil/oily acid yielding hydroxy functionalized polymers and Fe(II) species which reacted with hydroperoxide groups of the autooxidized polymers, according to the reaction shown below (Scheme 2).

GPC measurements of the hydroxy functionalized polymers were also carried out. M_n values of the hydroxy functionalized products had nearly the same M_n values with their starting polymers. Molecular weights of the autooxidized and hydroxy functionalized polymeric oils/oily acids are listed in Table 1.

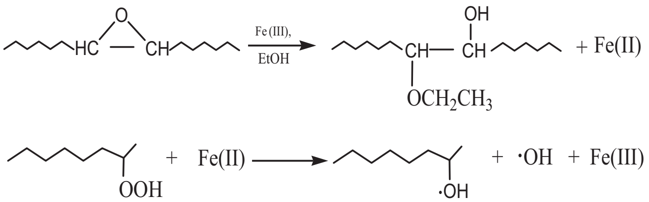
Table 1.
Molecular weights of the autooxidized and hydroxy functionalized oil/oily acids. (MWDs of the samples ranged from 1.2 to 1.7).

Entry	Alcohol*			M_n
	EtOH	$Et(OH)_2$	$G(OH)_3$	
PSyb-1				2600
PLina-1				950
PLnlna-1				1000
PSsm-1				2000
PSsmFe-1	+			2000
PSyb1Fe1	+			2300
PSyb1Fe2		+		2600
PSyb1Fe3			+	2500
Eps				2700
EpsFe-1	+			2600
EpsFe-2		+		3000
EpsFe-3			+	2800

*indicates the alcohols used in the synthesis of hydroxy functionalized polymers.

Hydroxy functionalized polymeric oils/oily acids were soluble in benzene, chloroform and THF. So, solvent cast polymer film in a Petri dish was obtained by casting from this solvent. The digital images of the polymeric oils are shown in Figure 2b and c. Psyb1Fes and PssmFes gave smooth and soft solvent cast films while PlinaFes and PLnlnas and commercial epoxidized soybean oils (EpsFe)s yielded viscous liquids. Soluble polymeric oil films of hydroxy functionalized soybean and sesame oil are promising materials to make further chemical modification reactions for the packaging film and biomedical applications.

^{1}H NMR and FTIR spectra of the hydroxy functionalized polymeric oils were also recorded. ^{1}H NMR spectrum of the hdroxy functionalized polymer was the same as the autooxidized starting polymer. So, this was not useful for the characterization of the hydroxy functionalized product. FTIR spectrum had the hydroxyl characteristic signal of the hydroxy functionalized polymers at around 3450 cm^{-1} as shown in the Figure 3 b. A new peak at 1630 cm^{-1} due to the carbonyl stretch was also observed. Presumably, carbonyl group could be formed, after the hydroperoxide was cleaved by Fe(II) salt during the ring opening of epoxide.



Scheme 2.
Ring opening and redox reactions of the epoxide and hydroperoxide groups of the polymeric oils/oily acids with Fe(III) and Fe(II) species, respectively.

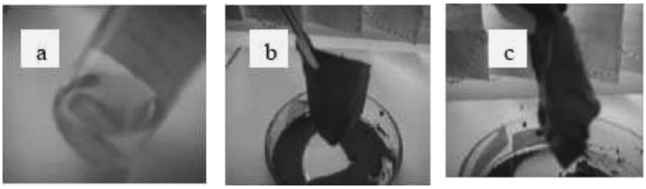


Figure 2.
The images of (a) autooxidized of soybean oil, and solvent cast films of hydroxy functionalized polymeric soybean oil (b), and hydroxy functionalized sesame oil (c).

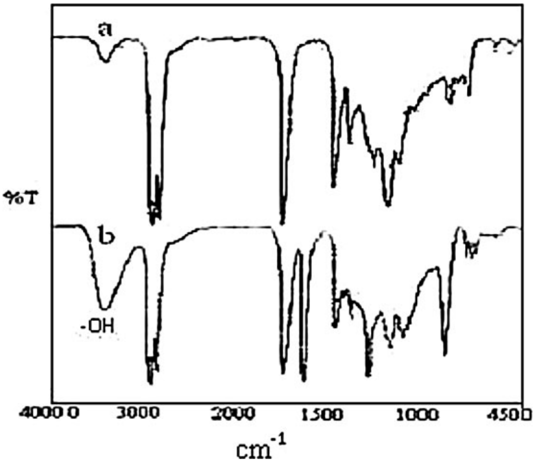


Figure 3.
FTIR spectra of the autooxidized (a) and hydroxy functionalized (b) polymeric soybean oil.

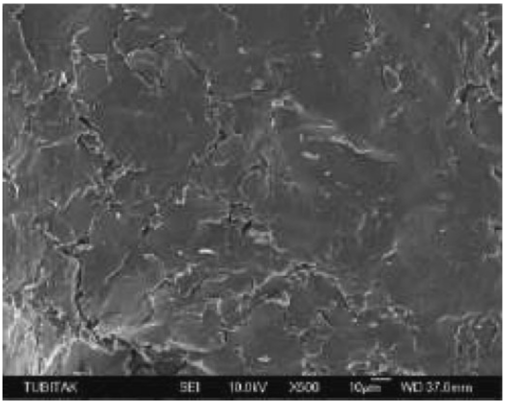


Figure 4.
SEM micrographs of the hydroxy functionalized soybean oil.

Table 2.
Adhesion force of the autooxidized polymeric oils/oily acids.

Entry	Adhesion force (N)
PLina-2	0.5
PLinlna-2	0.5
PSyb-2	3.0
PSsm-2	0.6
Post-it (commercial)	0.8

Scanning electron microscopy (SEM) was a crucial tool for studying surface topography of the samples. SEM micrographs indicated that the hydroxy functionalized polymers contained iron salt clusters ca. 1 μm size. Figure 4 shows the SEM micrographs of the hydroxy functionalized soybean oil.

The Adhesion Test of the Polymeric Oils/Oily Acids

Several polymers such as atactic polypropylene and natural rubber have post-it adhesive bulk properties.[23] Because the autooxidized oils were sticky, so, the post-it adhesive properties of the autooxidized and hydroxy functionalized polymeric oils/oily acids obtained in this work were studied. For this purpose, a simple device containing a dynamometer as shown in Figure 1 was used. A paper stuck with the oils/oily acids polymers on a glass plate was pulled away by using the dynomometer and the adhesion force at the moment that the paper pulled away from the glass plate was recorded. Adhesion forces of the polymeric oils/oily acids measured by this way are listed in Table 2. Autooxidized polymeric soybean oil had the highest adhesion force while unprocessed (Syb, Ssm, Lina, Lnlna) and hydroxy functionalized (Psyb-Fe-1, PSsm-Fe-1, PLina-Fe-1, Plnlna-Fe-1) oils/oily acids were found to be completely non-adhesive.

Conclusion

Autooxidized oils/oily acids were rearranged to the hydroxy functionalized polymeric oily/oily acids which were crucial to make further modification reactions to obtain new biomaterials based on the plant oils (e.g. polyurethanes). Solvent cast films of these hydroxy functionalized polymeric products were soft and soluble in common organic solvents which make them promising materials for packaging and biomedical applications.

Because of their sticky properties, autooxidized oils/oily acids can be used as post-it adhesive. Furthermore, the adhesion force of the autooxidized soybean oil was found to be four times higher than that of the commercial post-it.

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