

Synthesis of Photoactive Compounds from Tall Oil Fatty Acids

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Received: 29 November 2019; Accepted: 09 May 2020

Abstract: Photocurable systems are more effective, faster and require less energy than conventional thermal curing methods. To facilitate the ongoing transition toward a biobased economy, photoactive compounds were synthesized from tall oil fatty acids (TOFA) which is a by-product from wood pulping. In this study, photoactive monomers were synthesized by two different chemical pathways using oleic acid and TOFA as raw materials. Firstly, double bonds present in TOFA were epoxidized, followed by epoxy ring-opening with acrylic acid which introduced photoactive functional groups into the fatty acid backbone. Intermediates and final products were analysed using titration methods (acidic value, epoxy value, iodine value) and FTIR. The preferred final product (3-acryloyloxy-2-hydroxypropyl)-9-hydroxy-10-acryloyloxy-stearate (Acr-St) was synthesized by both pathways. In the case of oleic acid, a compound of Acr-St was yielded, while in case of TOFA, the Acr-St was present in mixture along with TOFA acryloyloxy derivatives (TOFA-acr.der.). The final products were photopolymerized using UV irradiation (396 nm) and as a photoinitiator 3 wt% solution of TPO (2,4,6-trimethylbenzoyl diphenylphosphine oxide) was used. However, only the synthesis using oleic acid yielded a photocurable compound.

Keywords: Photopolymerization; TOFA; acrylic acid; renewable materials

Abbreviations

Ol-Cl:	oleoyl chloride
Gl-St:	glycidyl-9,10-epoxystearate
TOFA-Cl:	TOFA chloride
EpTOFA-Gl-est:	epoxidized TOFA glycidyl esters
DMF:	N, N-dimethylformamide
DCM:	dichloromethane
A-OH:	allyl alcohol
TEA:	triethanolamine
HDAB:	hexadecyltrimethylammonium bromide
FTIR:	Fourier transform infrared spectroscopy
TOFA:	tall oil fatty acid
TPO:	2,4,6-trimethylbenzoyl diphenylphosphine oxide.



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1 Introduction

Plant oils have become an attractive alternative to petrochemicals in order to obtain different polymers and materials [1]. Plant oils are triglyceride mixtures with varying saturated and unsaturated fatty acid compositions. The composition of fatty acids varies depending on the plant species, growing conditions and other parameters. Different oil derivatives have been synthesized by oleochemistry and are used in resins, composites, coatings, adhesives, surfactants, lubricants, cosmetics, biomedical applications and also modified into useful polymeric materials such as polyester amides and polyurethanes [1–3].

The implementation of renewable resources in photopolymerization is perspective research field. Renewable materials may substitute petroleum-derived monomers in order to increase the environmental benefits of photopolymerization. Fatty acids and triglycerides derived from plant oils are particularly attractive starting materials for photopolymerization for two reasons—intrinsically high molecular weight and high functionality [3–4].

Fatty acids like oleic acid found in plant systems, are known to have special properties (for example, long fatty acid chains) thus fatty acids can be modified quite easily and used for different applications. Tall oil has been obtained for over a century as a by-product from wood pulping via Kraft process [5,6]. Tall oil usually contains ~51% of oleic acid and ~49% of linoleic acid. Oleic acid is unsaturated fatty acid $C_{18}H_{34}O_2$ with one double bond between 9th and 10th carbon atom [7]. Oleic acid is mostly found in tall oil and olive oil. TOFA is mostly used in the polyurethane industry, adhesives, as an emulsifier, resins, photocurable systems (used in material coatings) [1,8].

The functionalization of double bonds in fatty acids is carried out with different chemical modifications, the most widely used is epoxidation [3]. The opening of epoxy rings can be catalyzed in both acidic and basic environment, which provides the basis for different further reactions [9]. Epoxy rings in the epoxidized oils can be opened with different monomers, for example, acrylic acid, which is capable of further photopolymerization [9].

Different methods can be used to produce protective organic coatings. The design of the so-called 100% solid systems has resulted in significant reductions in volatile organic compound (VOC) emissions in the manufacture of coatings for different applications. Photo-induced polymerization is particularly efficient as it requires considerably lower energy input to produce polymer coatings compared to thermal curing schemes [4,10]. UV-curing systems have several limitations such as high material and equipment costs, and sensitivity to oxygen (free radical mechanism) and moisture (cationic curing mechanism) [11].

Photo-induced polymerization acrylates and different derivatives are widely used due to their high reactivity, which is significant for photocurable processes [11,12]. Acrylates actively homopolymerize by polymer chain-growing mechanism and are capable to link the hydrogen from monomers. Acrylated oligomers, mono- and multifunctional acrylates used in formulations adjust viscosity, rate of curing, crosslinking and characteristics of the material [11,12]. Another significant advantage of acrylates is their ability to photopolymerize in the presence of free radicals quite rapidly. Acrylates used for obtaining photocurable resins are described with multifunctional reactivity of double bonds in the same molecule [13].

The aim of this study is to synthesize photocurable monomer from renewable resources. Two different pathways of synthesis were applied. The first synthesis pathway employed oleic acid as a renewable feedstock, while in the second pathway tall oil fatty acids were used.

2 Materials and Methods

2.1 Materials

Allyl chloride (reagent grade, 98%), allyl alcohol (reagent grade, ≥99%), epichlorohydrin (reagent grade, ≥99%), acetic acid (reagent grade, 99,8%–100,5%), thionyl chloride (reagent grade, ≥99%),

hexadecyltrimethylammonium bromide ($\geq 98\%$), p-benzoquinone ($\geq 98\%$), ion exchange resin *Amberlite IR120* hydrogen form (acidic form) and oleic acid (technical grade) were purchased from *Sigma Aldrich*. Acrylic acid (stabilized with hydroquinone monomethyl ether) was purchased from *EMD Millipore Corporation*. Tall oil fatty acid *FOR2* was kindly provided by *Forchem Oyj*. Photoinitiator 2,4,6-trimethylbenzoyldiphenylphosphine oxide was purchased from *Lambson Ltd*. All reagents were used as received without further purification.

2.2 Methods

Products and intermediates were analysed with titrimetric methods—acid value according to ASTM D 1980-87 standard, epoxy value according to ASTM D 1652-04 standard, and iodine value according to ISO 3961:2013 standard. FTIR absorbance spectra were obtained in the infrared range from 4000 to 600 cm^{-1} with 32 scanning iterations and resolution of 4 cm^{-1} . Before each sample was tested, the background spectra were taken. FTIR data was obtained using *Thermo Scientific Nicolet iS50 FT-IR* spectrometer.

2.2.1 Titration Methods

Acid value (ASTM D 1980-87)

The acid value was measured according to ASTM D 1980-87 standard, but few derogations from the guidelines were done: 99.8% methanol was used instead of neutralized 95% ethanol (methanol's acid value was determined separately); phenolphthalein indicator was replaced with cresol red, because of its colour change at the stoichiometric point is more noticeable.

Preparation of cresol red indicator.

Cresol red (0.1 g) was weighed in a 100 ml measuring flask, followed by adding 50 ml of methanol. Crystals were dissolved and ethanol was poured in up to mark.

Preparation of potassium hydroxide KOH solution.

For determination of acid value, ~0.25 molar KOH standard solution was used. Potassium hydroxide KOH (28.05 g) were weighed in a 2 l measuring flask. Granules were dissolved in ~1 l of methanol, followed by pouring methanol up to mark and mixing the solution.

Standardization of KOH solution.

Potassium hydrogen phthalate (KHF) (~1.5 g) was weighed in a 250 ml conical flask and dissolved in 50 ml of methanol, followed by adding 5–7 drops of cresol red indicator. The mixture was titrated until the colour turned purple. The concentration of KOH solution was calculated by the following equation:

$$c_{\text{KOH}} = \frac{m_{\text{KHF}}}{M_{\text{KHF}} V_{\text{KOH}}} \quad (1)$$

c_{KOH} —concentration of KOH solution, mol/l;

m_{KHF} —the mass of potassium hydrogen phthalate, g;

M_{KHF} —the molar mass of potassium hydrogen phthalate, g/mol;

V_{KOH} —the volume used of KOH solution in the titration, l.

Titration was repeated at least 3 times to minimize possible error implantation.

The process of analysis

Sample (~1.5 g) was weighed in a conical flask (200 ml) followed by adding 50 ml of methanol and the sample was completely dissolved. Cresol red indicator was added (5–7 drops) and the mixture was titrated

with standardized 0.25 mol/l KOH solution until the colour of the mixture changed from yellow to purple. The acid value of methanol was also measured. The acid value was calculated by the following equation:

$$AV = \frac{V_{KOH} \times c_{KOH} \times M_{KOH}}{m_s} \quad (2)$$

AV–acid value, mgKOH/g;

V_{KOH} –used volume of KOH solution in the titration, l;

c_{KOH} –concentration of KOH solution, mol/l;

M_{KOH} –the molar mass of KOH, g/mol;

m_s –the mass of the sample, g.

Epoxy value (ASTM D 1652-04)

At first, the sample was dissolved in solvent dichloromethane (DCM). The solution was titrated with a perchloric acid standard solution in glacial acetic acid. The stoichiometric point was determined using crystal violet indicator by the colour change from dark blue to green.

Preparation of crystal violet indicator solution (0.1%)

Crystal violet (~0.1 g) was weighed in 100 ml measuring flask and followed by adding 50 ml of glacial acetic acid. Crystals were completely dissolved, and glacial acetic acid was poured up to mark.

Preparation of tetraethylammonium bromide (TEAB) solution (20%) in glacial acetic acid

TEAB (100 g) was dissolved in glacial acetic acid (400 ml). After analysis solution was kept closed in a dark place.

Preparation of HClO₄ solution (0.1 M) in glacial acetic acid

Glacial acetic acid (250 ml) was poured in 1 l measuring flask, followed by adding 70% HClO₄ (11 ml) and mixing. Then acetic anhydride was added (50 ml) and glacial acetic acid was poured up to mark and the solution was mixed. The solution was left aside for 18 hours.

Standardization of 0.1 M HClO₄ solution

Potassium hydrogen phthalate (~0.2 g) was weighed in a 200 ml conical flask. The crystals were dissolved in glacial acetic acid (50 ml) and crystal violet indicator was added (6 drops). The mixture was titrated with HClO₄ solution until the colour changed from dark blue to green and did not turn back at least 2 minutes. The concentration was calculated by the following equation:

$$c_{HClO_4} = \frac{m_{KHF} \times 1000}{204.2 \times V_{HClO_4}} \quad (3)$$

c_{HClO_4} –the concentration of HClO₄ solution in glacial acetic acid, mol/l;

m_{KHF} –the mass of potassium hydrogen phthalate KHF, g;

V_{HClO_4} –the used volume of HClO₄ solution in glacial acetic acid, ml.

The process of analysis

Sample (~0.2 g) was weighed in a conical flask (100 ml) and followed by adding dichloromethane DCM (10 ml). The sample was completely dissolved, followed by the addition of TEAB solution (5 ml) and crystal violet indicator (5–7 drops). The mixture was titrated with standardized 0.1 M HClO₄ solution until the colour changed from dark blue to green and remained unchanged for at least 30 seconds.

The percentual weight amount of epoxy groups in the sample was calculated by the following formula:

$$E = 4.3 \times V_{HClO_4} \times \frac{c_{HClO_4}}{m_s} \quad (4)$$

E—weight amount of epoxy, %;

V_{HClO_4} —used volume of $HClO_4$ solution in glacial acetic acid, ml;

c_{HClO_4} —the concentration of $HClO_4$ solution in glacial acetic acid, mol/l;

m_s —the mass of the sample, g.

The amount of epoxy groups can also be expressed as moles per gram:

$$E_g = \frac{V_{HClO_4}}{1000} \times \frac{c_{HClO_4}}{m_s} \quad (5)$$

E_g —the amount of epoxy groups in the sample, mol/g.

Iodine value (ISO 3961:2013)

Preparation of 15% potassium iodide KI solution

Potassium iodide (30 g) was weighed in Erlenmeyer flask (250 ml), followed by adding deionized water (170 ml) and dissolved. The flask was closed and stored in a dark place.

Sodium thiosulphate 0.1 M standard solution was prepared from a Fixanal ampoule.

Sample (~0.15 g) was weighed in conic flask (250 ml), followed by adding chloroform (10 ml) and dissolved. Hanus solution (25 ml) was added using Mohr pipette and the flask was closed immediately. The mixture was stirred and stored in a dark place for 60 minutes. After that, 15% KI solution (15 ml) and deionized water (100 ml) was added. The mixture was immediately titrated with 0.1 M sodium thiosulphate solution until the mixture turned colourless. Blank tests (without sample) were titrated likewise.

Iodine value was calculated by the following equation:

$$IV = \frac{(V_b - V_a) \times c_{Na_2S_2O_3} \times 0.1269}{m_s} \times 100 \quad (6)$$

JV—iodine value, $gI_2/100\text{ g}$;

V_b —the volume of $Na_2S_2O_3$ solution used in the blank test, ml;

V_a —the volume of $Na_2S_2O_3$ solution used in sample analysis, ml;

$c_{Na_2S_2O_3}$ —the concentration of $Na_2S_2O_3$ solution, mol/l;

0.1269—the mass of iodine (grams), which reacts with one millilitre 1 M $Na_2S_2O_3$ solution;

m_s —the mass of the sample, g.

2.3 Photocurable Monomer Synthesis from Oleic Acid (1st Pathway)

Idealized reaction scheme of 1st pathway of synthesis is depicted in Fig. 1. In this pathway initially, oleic acid chloride was obtained, then the allyl ester. The obtained ester was epoxidized and epoxy rings were opened using acrylic acid.

1st and 2nd Steps—obtaining allyl oleate from oleoyl chloride

The 2nd step of this pathway was performed right after the 1st because the intermediate obtained in the 1st step (oleoyl chloride) may hydrolyse with air humidity.

All the laboratory glassware involved in the allyl oleate synthesis were initially dried in the oven at 110° C and at first two $CaCl_2$ tubes were made. Oleic acid (150 ml, acid value 195.9 mg KOH/g) was poured into

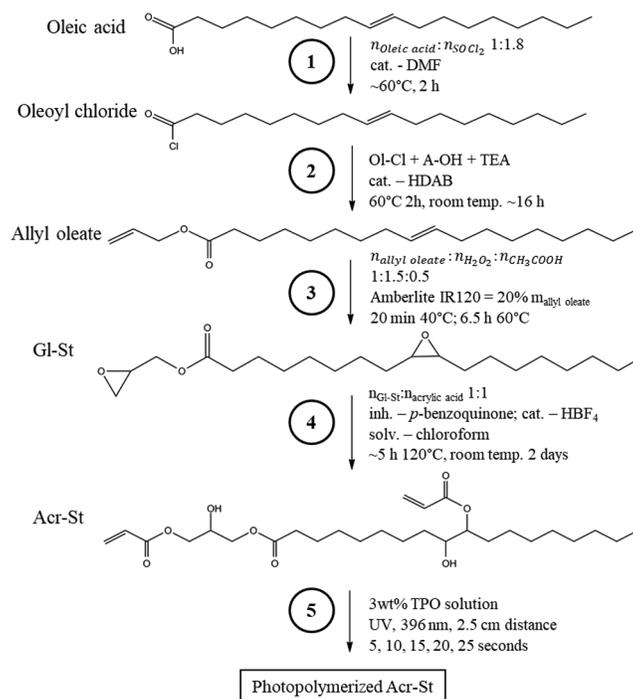


Figure 1: Idealized reaction scheme of monomer's synthesis from oleic acid

the dropping funnel, followed by adding 5 drops of DMF and closed with CaCl₂ tube. SOCl₂ (43 ml) was poured into the three-neck round bottom flask. Side-necks of the flask were closed with CaCl₂ tubes and a central neck was fitted with a sealed mechanical stirrer. The flask was immersed into a thermostatic water bath at 60°C and agitated with a mechanical stirrer at 230 rpm. One of the CaCl₂ tubes was exchanged to the dropping funnel, followed by dropwise addition of oleic acid to the flask in about 15 minutes. After oleic acid was completely added, the flask was closed with a CaCl₂ tube and synthesis was continued for about 2 h. Allyl alcohol (45 ml) and 73 ml of TEA were poured into another dropping funnel. One of the CaCl₂ tubes was exchanged to the dropping funnel and the allyl alcohol/TEA mixture was added dropwise to the flask in about 1 h. After addition, the funnel was exchanged back to CaCl₂ tube. The synthesis was continued for 2 h at 60°C and for about 16 h at room temperature, while stirring it at 150 rpm [14,15].

Purification of the product: 200 ml of chloroform and 200 ml of distilled water and few drops of cresol red was added to the mixture in the beaker. The layers were stirred with magnetic stirrer rather slowly to prevent mixing of both layers. Small amounts (~1 ml) of hydrochloric acid HCl was added to the mixture until the colour changed from violet to yellow. The bottom (organic) layer was transfused into a separating funnel and rinsed 3 times with 100 ml of distilled water. The resulting organic layer was further evaporated with a rotary evaporator starting at 600 mbar pressure and slowly reducing it to 10 mbar [14,15].

3rd Step—epoxidizing allyl oleate to form glycidyl-9,10-epoxystearate

Allyl oleate (32.46 g, 0.1 mol, iodine value 146.2 g I₂/100 g) was poured into three-necked round bottom flask followed by addition of acetic acid and ion exchange resin Amberlite IR120 hydrogen form in the required ratio (depicted in the scheme in Fig. 1). The flask was equipped with a mechanical stirrer mixed at 600 rpm and heated at 40°C in the thermostatic water bath. H₂O₂ (11.8 g, 35%) was weighed into a dropping funnel and added to the mixture in about 20 min. After that, the water bath was heated to 60°C and the synthesis was continued for 6.5 h [16].

Purification of the product: the reaction mixture was poured into a separating funnel, followed by addition of 50 ml of ethyl acetate and 30 ml of distilled water to the reaction mixture in the funnel. After extraction, the water layer was poured out with ion exchange resin. The organic layer was extracted with distilled water three more times, dried with anhydrous Na_2SO_4 and filtered. After that, the organic layer was evaporated at 60°C with a rotary evaporator at 180 mbar to get rid of ethyl acetate and at 10 mbar to completely dry the product [16].

4th Step—synthesis of final product Acr-St (3-acryloyloxy-2-hydroxypropyl)-9-hydroxy-10-acryloyloxystearate

GI-St (18.95 g, 0.05 mol, epoxy value 2.9 mmol/g), 0.06 g *para*-benzoquinone (polymerization inhibitor) and acrylic acid were added to the three-necked round bottom flask. The mixture was stirred at 400 rpm and heated at 60°C for about 5 h. The required amount of acrylic acid was added to the flask through the syringe, by adding 1 ml every 10 min. Chloroform (50 ml) and 5 drops of 50% HBF_4 were also added to the reaction mixture. The heating was turned off after about 5 h and a sample was taken to determine acid value, which was evaporated on rotatory evaporator at 10 mbar to remove chloroform. The synthesis continued for about 2 days stirring at 300 rpm. The sample was taken once a day to determine acid value [2,17].

Purification of the product: the reaction mixture was poured into a separating funnel. The organic layer was rinsed three times with 20 ml of saturated NaHCO_3 solution until no gas (CO_2) was released. The mixture was washed with 20 ml of distilled water and dried with anhydrous Na_2SO_4 . The mixture was filtered and evaporated at 60°C on a rotary evaporator at 600 mbar and slowly reducing the pressure to 10 mbar [2,17].

2.4 Photocurable Monomer Synthesis from Tall Oil (2nd Pathway)

In the second pathway, tall oil was used as a renewable feedstock. All the steps of synthesis were the same as for the 1st pathway. As the result, the mix of TOFA acrylated derivatives were obtained.

1st and 2nd Step—obtaining TOFA allyl esters from TOFA chlorides

Both syntheses were performed as mentioned previously in the synthesis description for the photocurable monomer from oleic acid. TOFA (50 g, acid value 192.1 mg KOH/g) was used. The ratios of SOCl_2 , allyl alcohol and TEA were the same [14,15].

3rd Step—epoxidation TOFA allyl esters to form EpTOFA-GI-est

Epoxidation was performed as mentioned previously using 45.00 g of TOFA allyl esters (0.34 mol, iodine value 193.2 $\text{gI}_2/100\text{ g}$) and needed amount (based on ratios depicted in Fig. 2) of acetic acid, ion exchange resin Amberlite IR120 hydrogen form and 35% H_2O_2 . The mixture was stirred at 500 rpm and heated at 40°C . H_2O_2 was added from dropping funnel in about 30 min. After the temperature reached 60°C , the reaction was continued for 7 h [16].

4th Step—synthesis of final product Acr-St (3-acryloyloxy-2-hydroxypropyl)-9-hydroxy-10-acryloyloxystearate

The synthesis of the final product was performed as mentioned previously using 35.10 g of EpTOFA-GI-est (0.09 mol, epoxy value 2. mmol/g) and 0.2 g of *para*-benzoquinone, and 6.7 ml of acrylic acid. Chloroform (88 ml) was used as a solvent and 18 drops of 50% HBF_4 were also added to the mixture. The mixture was stirred at 400 rpm and heated at 70°C for 6 h. After that, the heating was turned off and synthesis was continued at room temperature for about 18 h [2,17].

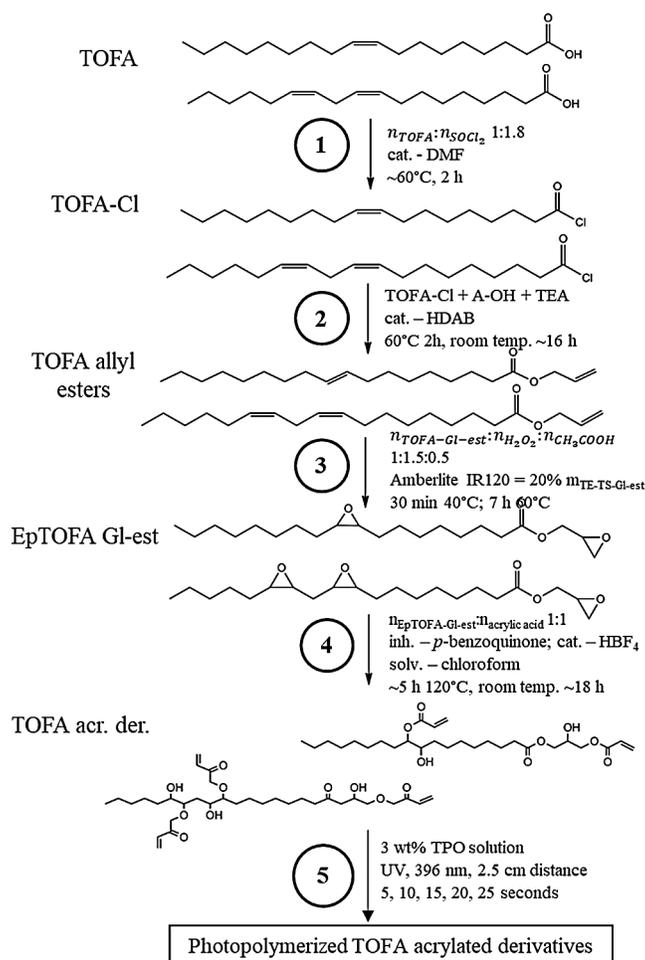


Figure 2: Idealized scheme of monomer's synthesis from TOFA

2.5 Photopolymerization of Samples (5th Step)

Both resulting products were photopolymerized in the presence of 2,4,6-trimethylbenzoyl diphenyl phosphine oxide (TPO) 3 wt% solution. The used amounts of samples and TPO are depicted in Tab. 1.

TPO was transferred to a dark bottle (50 ml) and dissolved in acetone. The monomer was added, and the mixture was stirred with a glass rod. A small amount of the mixture (1–2 drops) were put on a glass slide and the mixture was irradiated with UV light (wavelength 396 nm) at 2.5 cm distance for 5 seconds. The sample was touched with a metal plate to check if the sample has cured. After that, it was irradiated for 10, 15, 20 and 25 seconds and checked after each time period with a metal plate.

Table 1: Used amounts of TPO and sample for photopolymerization

Pathway of synthesis	Used amounts, g	
	TPO	Sample (final product)
1	0.05	1.5
2	0.03	9.0

3 Results and Discussion

Photocurable compounds derived from oleic acid and TOFA have been described using FTIR spectra and titration methods. It is important that the chosen renewable material does not compete with food industry. Similar compounds have been synthesized from different plant oils, e.g., castor oils [18,19], tung oil [20] and soybean oil [21] and their derivatives. The main reason why TOFA was chosen for this work is that very few photocurable compounds have been synthesized from this renewable material.

3.1 Characterization of Photocurable Monomer Synthesized from Oleic Acid and Its Intermediates

The FTIR spectra of obtained intermediates and final products are depicted in Fig. 3.

In the oleic acid spectra, the peak at 1706 cm^{-1} is characteristic to the stretching vibration of C=O bond which indicates the presence of carboxyl functional groups, but the peak at 3008 cm^{-1} is characteristic to =C–H bond which indicates stretching vibration of existing C=C double bonds.

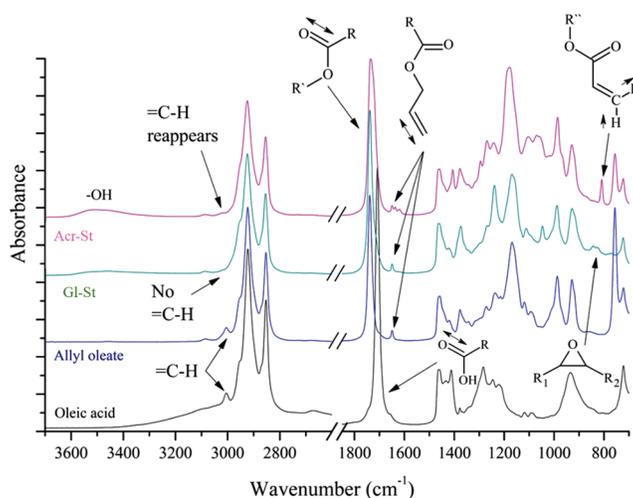


Figure 3: FTIR spectra of intermediates and final product of synthesis of the photocurable monomer from oleic acid

In the allyl oleate spectra, the peak at 1735 cm^{-1} is characteristic to the stretching vibrations of C=O bond which indicates ester functional groups, meanwhile peak at 3008 cm^{-1} can be assigned to the stretching vibrations of =C–H and peak at 1645 cm^{-1} is characteristic to C=C bond which indicates the stretching vibration of allyl ester functional groups specifically. This correlates with an increased iodine value (Tab. 2) indicating that the esterification reaction has taken place.

In the Gl-St spectra, the peak at 845 cm^{-1} is characteristic to an epoxy-functional group and =C–H double bonds stretching vibrations at 3008 cm^{-1} which are characteristic to oleic acid have disappeared.

Table 2: Titration data of samples obtained in synthesis of the photocurable monomer from oleic acid

Compound	Acid value, mg KOH/g	Epoxy value, mmol/g	Iodine value, gI ₂ /100 g	Yield, g	Yield, %
Oleic acid	195.9	–	90.6	–	–
Ol-Cl	–	–	–	–	–
Allyl oleate	16.5	0.04	146.2	177.1	96.5
Gl-St	–	2.9	65.2	21.1	59.3
Acr-St	25.5	0.1	85.4	14.8	51.9

There is a peak at 1645 cm^{-1} which indicates stretching vibrations of C=C double bonds and according to the iodine value data from Tab. 2, it can be concluded that the compound contains allyl ester C=C double bonds. Meanwhile, the epoxy value has increased therefore from these results it can be concluded that the epoxidation has occurred partially. The C=C double bond of allyl esters is conjugated, thus decreasing its reactivity.

In the Acr-St FTIR spectra, the stretching vibrations of epoxy rings at 845 cm^{-1} have disappeared. This correlates with epoxy value data from Tab. 2 which also shows that the epoxy value has decreased. Therefore, it can be inferred that the epoxy rings have opened. The increase of iodine value (comparing to GI-St) and peak at 810 cm^{-1} indicates out of plane deformation vibrations of =C-H bonds which is characteristic to acrylic acid ester, which proves that the epoxy rings have been opened with acrylic acid. The opening of epoxy rings is also confirmed by stretching vibrations at 3500 cm^{-1} which indicate the curve of OH functional groups.

The final product from this synthesis did photopolymerize, therefore the FTIR spectra of Acr-St mixture with TPO irradiation with UV light for 5, 10, 15, 20 and 25 seconds was obtained, which is depicted in Fig. 4. The peak at 810 cm^{-1} indicates out of plane deformation vibrations of =C-H bonds (characteristic to acrylic acid ester) disappeared after 10 seconds, which proves that the curing reaction undergoes through acrylic ester moiety. The peak at 1645 cm^{-1} indicates stretching vibrations of conjugated vinyl ester groups, which refers that vinyl ester functional groups do not involve in this polymerization.

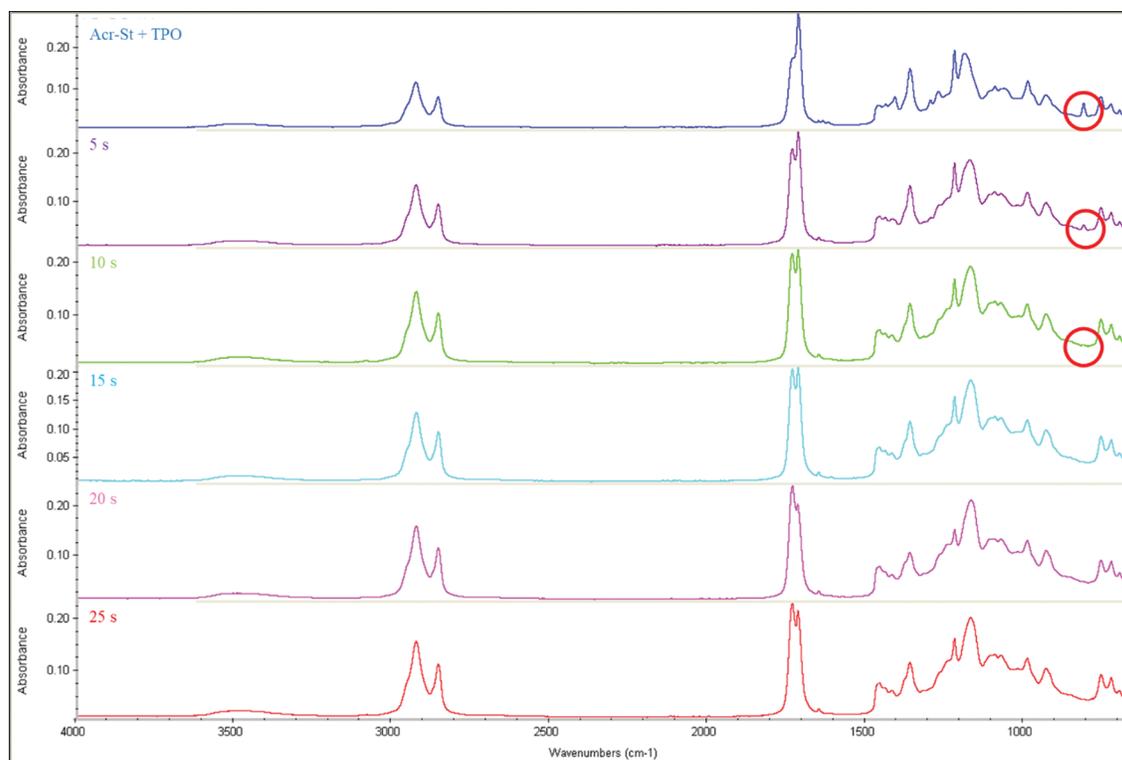


Figure 4: FTIR spectra of monomer's synthesized from oleic acid photopolymerization

3.2 Characterization of Photocurable Monomer Synthesized from Tall Oil and Its Intermediates

The FTIR spectra of obtained intermediates and final products are depicted in Fig. 5.

In the spectra of TOFA, the peak at 1706 cm^{-1} indicates of stretching vibrations of C=O double bonds which are characteristic to carboxyl groups, and peak at 3008 cm^{-1} indicates of stretching vibrations =C-H bonds in TOFA.

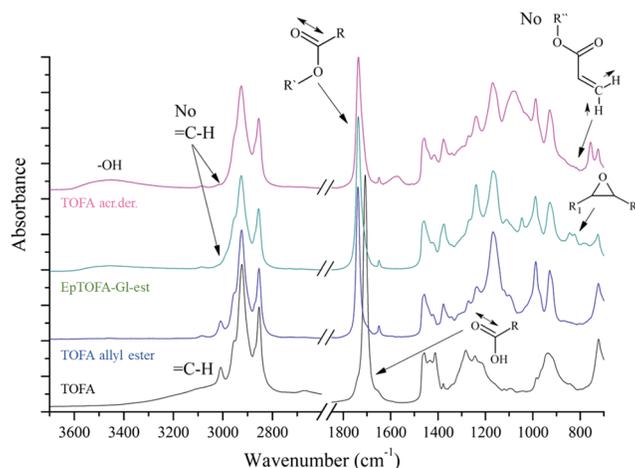


Figure 5: FTIR spectra of intermediates and final product of synthesis of the photocurable monomer from TOFA

The peak at 1735 cm^{-1} in TOFA allyl ester spectra indicates of stretching vibrations of C=O double bonds which indicates ester functional groups, also peak at 1635 cm^{-1} indicates stretching vibrations of C=C double bonds which indicate allyl ester, functional groups. These data correlate with an increased iodine value (Tab. 3), therefore it can be concluded that the reaction has occurred, and the intermediate is allyl ester.

The peak at 845 cm^{-1} in spectra of EpTOFA-GI-est indicates of stretching vibrations of epoxy rings. There is also visible peak at 1635 cm^{-1} which indicates of stretching vibrations of C=C double bonds which are characteristic to allyl ester functional group. Data from Tab. 3 shows that the epoxy value has increased but the presence of allyl ester peak in spectra shows that the epoxidation has occurred partially, the high iodine value demonstrates that too.

Table 3: Titration data of samples obtained in synthesis of the photocurable monomer from TOFA

Compound	Acid value, mg KOH/g	Epoxy value, mmol/g	Iodine value, gI ₂ /100 g	Yield, g
TOFA	192.1	–	147.5	–
TOFA-Cl	–	–	–	–
TOFA allyl ester	9.2	0.09	193.2	53.6
EpTOFA-GI-est	–	2.9	75.9	45.1
TOFA acr.der.	8.8	0.4	76.9	22.3

The peak at 810 cm^{-1} in spectra of TOFA acryloyloxy derivatives does not indicate of plane deformation vibrations of =C–H bond, which is characteristic to acrylic acid ester, as the synthesis of the monomer from oleic acid. Low epoxy value (Tab. 3) proves that the epoxy rings have been opened, but since the iodine value has changed only a little, it can be inferred that the rings haven't been opened with acrylic acid. The photopolymerization of this sample was unsuccessful.

4 Conclusions

- Unsaturated fatty acids such as oleic acid derived from plants are appropriate raw material for synthesis of the photoactive compounds.

- Monomer synthesized from oleic acid was cured when exposed to UV light, thus it can be used for photopolymer material development. FTIR spectra during photopolymerization reaction confirmed that the material is cured using acrylic acid moieties that have been introduced into the backbone of oleic acid.
- The final product obtained from TOFA did not photopolymerize due to the lack of the acrylic acid moieties. The oxirane ring-opening reaction with acrylic acid should be optimized to avoid undesired side reactions

Funding Statement: The research leading to these results has received funding from the European Regional Development Fund Contract No. 1.1.1.5/ERANET/18/03, as part of the jointly funded European M-ERA-NET project Bio4Cryo, “Development of Biobased Cryogenic Insulation Modified with Nanocrystalline Cellulose”.

Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

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