



HAL
open science

Linseed Oil-Based Thermosets by Aza-Michael Polymerization

Yvan Ecochard, Rémi Auvergne, Bernard Boutevin, Sylvain Caillol

► **To cite this version:**

Yvan Ecochard, Rémi Auvergne, Bernard Boutevin, Sylvain Caillol. Linseed Oil-Based Thermosets by Aza-Michael Polymerization. *European Journal of Lipid Science and Technology*, 2020, Special Issue: Fats and Oils as Renewable Feedstock for the Chemical Industry, 122, pp.1900145-1900153. 10.1002/ejlt.201900145 . hal-02356795

HAL Id: hal-02356795

<https://hal.science/hal-02356795>

Submitted on 15 May 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Linseed oil-based thermosets by Aza-Michael polymerization

Yvan Ecochard,^a Rémi Auvergne,^a Bernard Boutevin,^a Sylvain Caillol^{a*}

^a ICGM, UMR 5253 – CNRS, Université de Montpellier, ENSCM, 240 Avenue Emile Jeanbrau 34296 Montpellier, France

*Corresponding author: Sylvain Caillol, Email: sylvain.caillol@enscm.fr

Keywords: Aza-Michael; Linseed oil; Acrylate; Amine; Thermosets

Running title: Aza-Michael addition on acrylated linseed oil

Abbreviations: **AEO**, Acrylated Epoxidized Oil; **AESO**, Acrylated Epoxidized Soybean Oil; **AELO**, Acrylated Epoxidized Linseed Oil; **ELO**, Epoxidized Linseed Oil; **MXDA**, *meta*-xylylenediamine; **PPG**, Polypropylenglycol; **NMR**, Nuclear Magnetic Resonance **TGA**, Thermogravimetric Analysis; **DSC**, Differential Scanning Calorimetry; **DMA**, Dynamical Mechanical Analysis; **FTIR**, Fourier Transform Infrared Spectroscopy; **SI**, Swelling Index; **GC**, Gel Content; **EEW**, Epoxy Equivalent Weight; **AHEW**, Amine Hydrogen Equivalent Weight; **AEW**, Acrylate Equivalent Weight; **GPC**, Gel Permeation Chromatography.

ABSTRACT

Aza-Michael addition on acrylated linseed oil (AELO) was performed to synthesize bio-based bulk thermosets without any catalyst. First, acrylation of epoxidized linseed oil (ELO) allowed to obtain acrylate functions with vicinal hydroxyl groups which enhanced the reactivity of acrylates. The autocatalytic effect of hydroxyl groups on acrylate monomers was highlighted by kinetic studies monitored by NMR and FTIR analyses on model molecules. Then, Priamine 1071, amine terminated poly(propyleneoxide) (PPO) and *meta*-xylylenediamine (MXDA) were used as cross-linkers with AELO. Curing kinetics were studied by DSC analyses to compare the reactivity of these structures. Priamine 1071 showed the highest reactivity; curing at room temperature was performed and high conversion was reached. Two enthalpies were observed with MXDA and only one at high temperature for PPO-based materials. Thermosets with a large range of mechanical properties were finally obtained from soft materials with PPO-diamine to hard materials with MXDA.

Practical applications: Thermosets were obtained by curing AELO with various diamines *via* aza-Michael reaction. Model reaction allowed to demonstrate catalytic effect of hydroxyl groups on Aza-Michael reaction of acrylated oil with amines. Hence, linseed oil is a promising resource in terms of sustainable development in polymer science.

INTRODUCTION

In a context of sustainable development, the depletion of petroleum resources and the use of hazardous products have led to consider new synthetic pathways toward more eco-friendly toxic polymers. As renewable resources, vegetable oils appear as interesting alternative building blocks. Their strong interest lies in their wide availability, low cost and low toxicity towards human and environment.[1-4] The nature of the vegetable oils as well as the cultivation conditions strongly affect the structure of triglycerides.[5] A large panel of structures is thus available with a various number of unsaturations, presence of dangling hydroxyl groups and even epoxy functions.[5] Triglycerides contained in vegetable oils are easily functionalized *via* their double bonds to synthesize various monomers of high functionality which directly gives access to bio-based cross-linked polymers.[3]–[9] Moreover, triglyceride monomers with epoxy,[10], [11] hydroxyl,[12] cyclocarbonate,[13]

amine,[14] siloxane[15], [16] or acrylate groups[17]–[21] can be obtained. Epoxidized triglyceride are synthesized through enzymatic process or organic pathway using $\text{H}_2\text{O}_2/\text{HCOOH}$ and are commercially available.[10], [11]

The Michael addition between a nucleophile and an acrylate have drawn much attention due to several advantages. Indeed, this reaction requires mild conditions, high degrees of conversion are easily reached and a large number of commercial monomers is available. This reaction have been widely used to synthesize polymers of varied structures which found utilization in a wide range of applications such as adhesives, coatings, additives, chemical synthesis or bio-medical applications.[22]–[26] Different functional groups are used as donors such as alcohol, amines and thiols. Highly functional monomers are however necessary to afford high performance thermosets. To this extent, vegetable oils are thus interesting candidates. Acrylated epoxidized oils (AEO) are easily obtained by ring opening reaction of epoxides with acrylic acid. This reaction leads to acrylate functions with a vicinal hydroxyl group on the aliphatic chain. AEOs have been widely used *via* free radical polymerization to synthesize thermosets.[17]–[21] Various free radical initiator systems have been explored such as thermal[27], [28] or UV[29], [30] initiators along with kinetics studies of curing. Thermosetting foams have also been synthesized from acrylated epoxidized soybean oil (AESO) and carbon dioxide using peroxide as free radical initiator.[31] Furthermore, cross-linking of AEOs was also be performed by Michael reaction. Wang *et al.* especially studied the thia-Michael reaction to synthesize UV-curable thermosetting AESO and studied the effect of different thiols on thermoset properties.[32] Kasetaitė *et al.* synthesized acrylate-thiol thermosets by addition of various thiols on AESO by thermal activation.[33] They compared thermal and mechanical properties of polymers cured with thiols with various functionalities from 2 to 6. The addition of amine to hyperbranched sucrose-soyate *via* aza-Michael reaction have been performed by Webster's group.[34] They especially studied the effect of the solvent, the ratio, the use of catalysts and different cross-linkers on coatings properties. However, no bulk thermosets have yet been reported *via* aza-Michael reaction on AEO. Furthermore, hydroxyl groups are known to improve reactivity by intermolecular activation *via* hydrogen bonds. The use of such activated structure can improve reactivity and allow to perform polymerization in mild conditions in order to avoid any catalyst or high temperature. This autocatalytic and sustainable monomer is thus very attractive in terms of green chemistry.

Therefore the present paper reports the study of reaction between amine and acrylated epoxidized linseed oil (AELO) without neither solvent nor catalysts. A first study was performed on model molecules to highlight the strong reactivity of AELO with amines and to identify the role of hydroxyl groups. Amines with various structures were then chosen to study reactivity with AELO by differential scanning calorimetry (DSC) and to afford bulk thermosets after curing. Physico-chemical and thermo-dynamical characterizations were finally performed to compare these materials.

EXPERIMENTAL PART

Materials

Acrylic acid, triphenylphosphine, hydroquinone, octylamine, 2-hydroxyethyl acrylate, butyl acrylate and benzophenone were purchased from Sigma-Aldrich. Ethyl acetate (EtOAc) was purchased from VWR. Epoxidized linseed oil (Vikoflex 7190, EEW = 167 g/eq.) was obtained from Arkema. Priamine 1071 was obtained from Croda. PPG-diamines (D2000, Mn \approx 2,000 g/mol; D400, Mn \approx 400 g/mol) were obtained from Huntsman. *Meta*-xylylenediamine (MXDA) was purchased from CeTePox. All materials were used as received. Deuterated solvent CDCl₃ was obtained from Eurisotop for NMR studies.

Nuclear Magnetic Resonance analyses (NMR): Proton nuclear magnetic resonance (¹H NMR) analyses were performed in deuterated chloroform (CDCl₃) using a Bruker Avance 400 MHz NMR spectrometer at a temperature of 25 °C. NMR samples were prepared as follows: 10 mg of product for ¹H experiment in around 0.5 mL of CDCl₃. The chemical shifts were reported in part per million relative to tetramethylsilane.

Thermogravimetric Analyses (TGA) were performed using a TG 209F1 apparatus (Netzsch) at a heating rate of 10 °C/min. Approximately 10 mg of sample was placed in an aluminium crucible and heated from room temperature to 550 °C under nitrogen atmosphere (60 mL/min).

Differential Scanning Calorimetry (DSC) analyses were carried out using a NETZSCH DSC200F3 calorimeter. Constant calibration was performed using indium, *n*-octadecane and *n*-octane standards. Nitrogen was used as the purge gas. Approximately 10 mg of sample was placed in perforated aluminum pans and the thermal properties were recorded between -100 °C and 200 °C at 20 °C/min to observe the glass transition temperature (T_g). The T_g values were measured on the second heating ramp to erase the thermal history of the polymer. All the

reported temperatures are mean values. T_{g0} (T_g at $t = 0$) of the mixture was calculated using the Equation 1.

$$\text{Equation 1} \quad \frac{1}{T_{g0}} = \frac{1}{T_{g1}} + \frac{1}{T_{g2}}$$

T_{g0} : Glass transition temperature of the mixture at $t = 0$ (before cross-linking); T_{g1} : Glass transition temperature of the acrylate; T_{g2} : Glass transition temperature of the amine.

Dynamic Mechanical Analyses (DMA) were carried out on Metravib DMA 25 with Dynatest 6.8 software. Samples were tested according to uniaxial tension mode while heating at a rate of 3 °C/min from $\approx T_g - 100$ °C to $T_g + 100$ °C, at a frequency of 1 Hz with a fixed strain of 10^{-5} m. These conditions have been chosen to study the elastic behavior of the materials.

Fourier Transform Infrared Spectroscopy (FTIR): Infrared (IR) spectra were recorded on a Nicolet 210 Fourier transform infrared spectroscopy spectrometer. Material samples were characterized by attenuated total reflection (ATR). For kinetic measurements a mixture of acrylate and amine was previously prepared in a mold and a droplet was introduced between two KBr tablets (evaporation of products can occur with ATR accessory). FTIR spectrums were recorded by transmission analysis for 120 minutes at room temperature. The characteristic IR absorptions mentioned in the text are reported in cm^{-1} .

Titration of the acrylate equivalent weight by ^1H NMR: The acrylate equivalent weight (AEW) is the amount of product needed for one equivalent of reactive acrylate function. It was determined by ^1H NMR using an internal standard (benzophenone). A known weight of product and benzophenone was poured into an NMR tube and 500 mL of CDCl_3 were added. It was determined using the Equation 2 by comparing the integral of the protons of the benzophenone and the integral of the acrylate moiety.

$$\text{Equation 2} \quad AEW = \frac{\int_{\text{PhCOPh}} * H_{\text{acrylate}}}{\int_{\text{acrylate}} * H_{\text{PhCOPh}}} * \frac{m_{\text{acrylate}}}{m_{\text{PhCOPh}}} * M_{\text{PhCOPh}}$$

\int_{PhCOPh} : integration of the benzophenone protons; \int_{acrylate} : integration of the protons of the acrylate function; H_{acrylate} : number of protons of the acrylate function; H_{PhCOPh} : number of protons of the benzophenone; m_{acrylate} : weight of the product; m_{PhCOPh} : weight of the benzophenone; M_{PhCOPh} : molecular weight of the benzophenone

Cross-linking density: From rubber elasticity theory,[35] the uniaxial stretching was studied on the rubbery plateau at $T > T_{\alpha} + 50$ ($T = 100$ °C for all materials), and at very small

deformations. Under these hypotheses, the cross-linking density (ν'), can be obtained from Equation 3, where E' is the storage modulus (Pa), R is gas constant ($8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$) and T_α is the temperature, in K, of transition from vitreous to rubber domain of material determined at the maximum of the $\tan \delta$ curve. Calculated values are given for information purposes and can only be compared.

$$\text{Equation 3} \quad \nu' = \frac{E'_{at T_\alpha+50}}{3RT_{\alpha+50}}$$

Swelling Index (SI): Three samples of around 30 mg each were separately put in THF for 24 h. The swelling index was calculated using the Equation 4 where m_2 is the mass of the material after swelling in THF and m_1 is the initial mass of the material.

$$\text{Equation 4} \quad SI = \frac{m_2 - m_1}{m_1} \times 100$$

Gel Content (GC): After SI measurements, the three samples were dried in a ventilated oven at 70°C for 24 h. The gel content was calculated using the Equation 5, where m_3 is the mass of the material after drying and m_1 is the initial mass of the material.

$$\text{Equation 5} \quad GC = \frac{m_3}{m_1} \times 100$$

Synthesis of Acrylated linseed oil

In a round bottom flask, epoxidized linseed oil (20g, 0.12 mol of epoxy functions), acrylic acid (34.52 g, 0.48 mol), hydroquinone (0.02 g) and triphenylphosphine (0.2 g) are heated at 80°C for 24 h. The flask is covered with aluminum paper to avoid UV exposure. When the reaction was complete, the mixture was diluted with 200 mL of ethyl acetate and washed three times with 100 mL of saturated sodium bicarbonate (NaHCO_3) solution and one time with brine solution (100 mL). The organic layer was dried with anhydrous magnesium sulfate and filtered. The solvent was extracted under vacuum and the pure product was obtained as a yellow viscous oil (quantitative yield).

Kinetics measurements on model molecules

Hydroxyethyl acrylate (1.8 g, 2 eq.) and octylamine (1 g, 1 eq.) was mixed in a round bottom flask with mechanical stirring at room temperature (25°C).

Butyl acrylate (2 g, 2 eq.) and octylamine (1 g, 1 eq.) was mixed in a round bottom flask with mechanical stirring at room temperature (25°C).

A first droplet was collect for FTIR measurements after good homogenization. A droplet was collect at different time and analyze through NMR analysis.

Material syntheses

Several formulations were carried out using AELO and different amines. In order to prepare the materials, the mass of amine was calculated using the Equation 6. The amine hydrogen equivalent weight (AHEW) and the acrylate equivalent weight (AEW) represent the amount of product needed for one equivalent of reactive function.

$$\text{Equation 6} \quad m_{\text{amine}} = \frac{\text{AHEW}_{\text{amine}} \times m_{\text{acrylate}}}{\text{AEW}}$$

The materials were synthesized with a molar ratio acrylate/amine of 2:1. Indeed, two acrylate react with each hydrogen of the primary amine. This ratio have been evaluated by DSC studies. The amine and the acrylate were stirred using a SpeedMixerTM under vacuum and then the homogeneous mixture obtained was put in a silicone mold for 24 hours at room temperature for all materials. A post-curing was performed at 150 °C for 1 h for AELO+MXDA and at 100 °C for 2 h and then 150 °C for 1 h for D2000 and D400-based materials.

RESULTS AND DISCUSSION:

AELO synthesis

Acrylated epoxidized linseed oil was synthesized by ring opening reaction of epoxides with acrylic acid (Figure 1) with quantitative yield. ¹H-NMR spectra of ELO and AELO are shown in SI-Figures 1 and 2. The conversion of epoxides into acrylate functions was monitored by ¹H-NMR analysis. The disappearance of epoxy protons at 2.84-3.21ppm was followed by appearance of acrylate functions at 5.85, 6.10 and 6.40 ppm. The number of acrylate functions was characterized by NMR titration with an internal standard. The measured value of AEW_{exp} for AELO is 380 g/eq. The theoretical value of AEW_{th} is 239 g/eq. (EEW of ELO + M_{acrylate} = 167 + 72 = 239). The activation of epoxy functions with triphenylphosphine causes also side-reactions such as epoxy homopolymerisation or epoxy-hydroxyl reactions. Less epoxy functions are thus available to react with acrylic acid addition. These side-reactions are responsible of oligomerisation and explain the difference of AEW between experimental and theoretical values. This can also explain the presence of many peaks between 3 and 3.5 ppm in ¹H-NMR spectrum. Epoxidized linseed oil has an average value of 6 epoxy functions per

triglycerides molecule. Thus, around 3 epoxy functions per molecule are involved in these side-reactions. Oligomerisation has already been observed in such monomers by GPC measurements.[36] Improvement in terms of reaction parameters might limit these side-reactions. Indeed, other type of catalyst such as chromium-based catalyst (AMC-2), are known to promote epoxy ring opening while minimizing epoxy homopolymerization.[36], [37] However, these catalyst are toxic. Moreover, in the present study, oligomerization is not a drawback since we target the synthesis of thermosets, therefore, we chose cleaner catalyst, despite side-reactions. AELO has also been characterized by FTIR spectra (SI-Figure 8). The peaks at 1620, 1400 and 800 cm^{-1} correspond to the $\text{CH}=\text{CH}_2$ vibration of acrylate function.

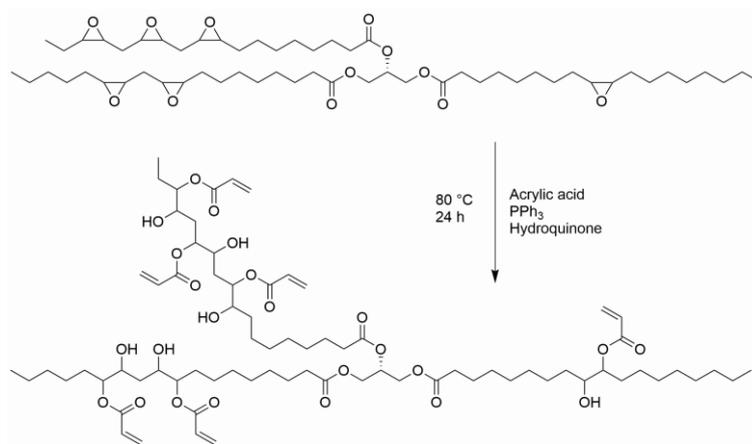


Figure 1. Acrylation of epoxidized linseed oil

Determination of the optimized formulation for materials

In order to determine the best formulation ratio, the optimum stoichiometry between acrylated linseed oil and amines was determined by DSC (maximum glass transition temperature of cured materials). Thermosets were obtained as bulk materials without the use of solvent. AELO was cured with Priamine 1071 at room temperature for one day. With a theoretical value of 2:1, the ratio between acrylate and amine functions was studied between 1:1 and 3:1. This ratio corresponds to the stoichiometry between each double bond of the acrylate and each amine function (NH_2). The highest T_g corresponds to the material with the optimum network, having the highest cross-linking density and thus the less unreacted free functions. The variation of the T_g , measured during the second DSC run, is plotted versus the Acrylate/Amine ratio in Figure 2. The optimum ratio is of 2 acrylate functions for 1 amine function. The discrepancy between the results are however low. The experimental ratio fits with the theoretical value (2:1) and was therefore chosen. Webster *et al.* studied the influence of the molar ratio between acrylated sucrose soyate and amines from 1:1 to 3:1 on material properties.[34] They selected a ratio of 1:1.5 as optimum. However, they worked on coatings

and their materials were formulated with catalyst and solvent. Therefore with such difference of conditions, the comparison is not relevant.

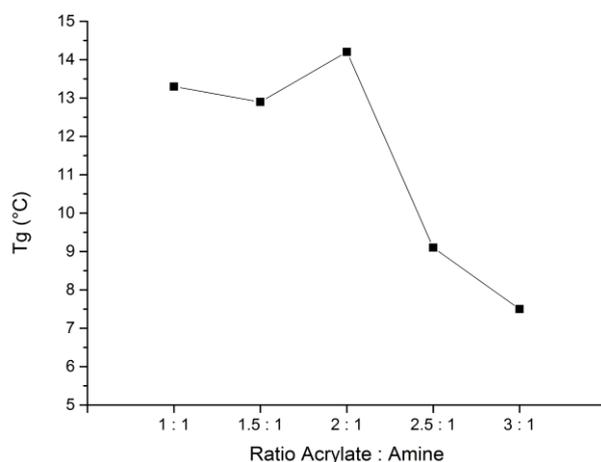


Figure 2. Evolution of glass transition temperature (T_g) versus acrylate:amine ratio for AELO + Priamine 1071 materials

Acrylate reactivity

Primary amines can react with two equivalents of acrylate function.[22] Yet the kinetic of these two reactions are not the same. The competition between the addition of the secondary amine versus the primary amine strongly depends on the steric and electronic environment of the amine.[34], [38] Despite its higher reactivity, the steric hindrance slows down the addition of the secondary amine which tends to be therefore slower than the addition of the primary amine. Indeed, Liu *et al.* have shown that linear aliphatic amines having high reactivity change the reactivity to primary amine > secondary amine. Only the primary amine tends to react without particular activation such as high temperature, high pressure or catalysts.

Yet the substituent on the acrylate monomer can have a strong impact on its reactivity towards amine functions. Thus, to highlight the influence of hydroxyl functions close to acrylates on aza-Michael reaction, a kinetic study was performed. In order to model the structure of AELO and to work on soluble molecules (avoiding cross-linking), monofunctional molecules were used in model reaction. Hydroxyethyl acrylate was thus chosen and compared with butyl acrylate as a linear aliphatic acrylate monomer. These two monomers were reacted with octylamine with a ratio of 2 acrylates for 1 amine as previously demonstrated. The reactions were monitored by NMR and FTIR analyses. NMR spectra of hydroxyethyl acrylate, butyl

acrylate and octylamine are shown SI-Figure 3-5. The conversion of acrylate functions has been plotted versus reaction time in Figure 3 for NMR and FTIR measurements.

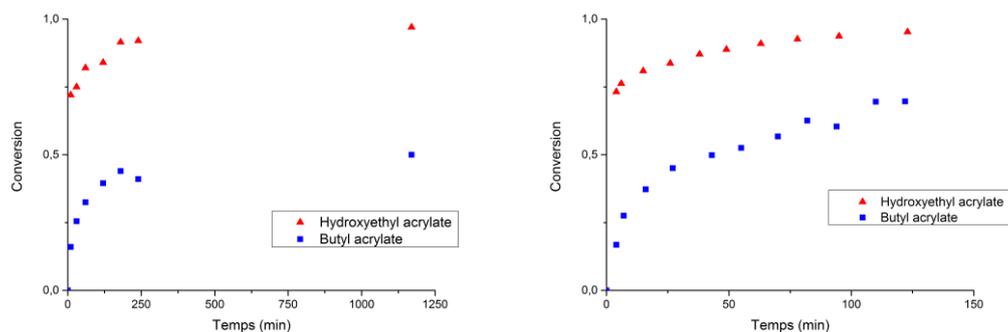


Figure 3. Hydroxyethyl acrylate and butyl acrylate conversion by reaction with octylamine (at 25 °C) followed by NMR (left) and FTIR (right) analyses

For NMR measurements, the disappearance of the double bonds of acrylate between 5,8 and 6,5 ppm was monitored for one day. The plots of the NMR spectra over time are shown in SI-Figures 6 and 7. The FTIR analyses were monitored by transmission to observe the disappearance of acrylate bonds at 1600 cm^{-1} for 120 min. FTIR spectra of monomers are shown in SI-Figures 9 and 10.

NMR and FTIR measurements highlighted the higher reactivity of the hydroxyethyl acrylate with octylamine compare to the butyl acrylate/amine couple. The kinetic is particularly fast for both acrylates but the main difference lies in the conversion. Indeed, a total conversion is reached with hydroxyethyl acrylate after 2 hours whereas only a limited conversion, around 50 %, is reached with the butyl acrylate even after two days. Such results indicate the very slow addition of the formed secondary amine onto the butyl acrylate. Thus, the hydroxyl function strongly increases the reactivity of the formed secondary amine and allows to reach total conversion with neither catalyst nor high temperature. Indeed, hydroxyl functions could form hydrogen bonding with the carbonyl of acrylate, which become more electro-attractor whereas the vinyl becomes more electrophile towards the amine attack. The hydroxyl activation of acrylates toward amines have also been observed by Sanui *et al.* with amino alcohols.[39] The distance between the amino and the hydroxyl groups had no impact on the reaction rate. Thus Sanui *et al.* concluded than the activation was due to intermolecular interactions. These observations suggest the same behavior in terms of activation for the hydroxyl acrylate structure of AELO. A slight difference between NMR and FTIR

measurement is observed for butyl acrylate kinetics, which could be explained by imprecision due to superimposition of peaks.

The structure of AELO is thus very interesting regarding the kinetics of the Michael reaction. The use of amine with high reactivity for Michael addition with this activated acrylate can prevent the use of catalyst or high temperature to achieve high conversion.

Reactivity with different amines

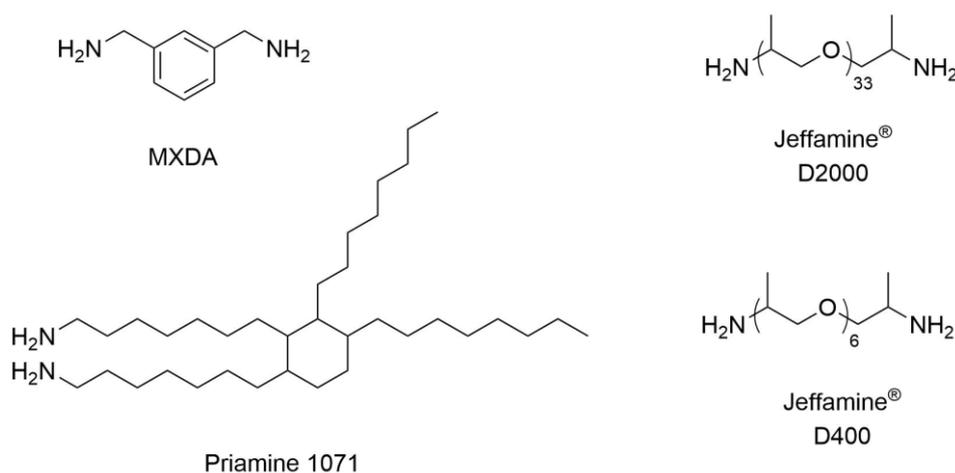


Figure 4. Amines structures

Four different amines have been chosen to synthesize thermosets by aza-Michael reaction (Figure 4). These amines were chosen for their difference in terms of reactivity and structure in order to obtain materials with various mechanical properties. Priamine 1071, D2000, D400 and MXDA present various substituents which could have an influence on the reactivity of the amine. Fatty acid dimer-based Priamine 1071 is a diamine with a long aliphatic chain, whereas D2000 and D400 have a poly(propyleneoxide) PPO structure. Finally the MXDA is an aromatic benzylic diamine. Kinetics of reaction between AELO and these amines were firstly studied by DSC analyses (Figure 5). Kinetics study with D400 was not performed due to its similarity with D2000 in terms of structure and reactivity. Long aliphatic diamines of different length were chosen in order to obtain soft materials whereas aromatic MXDA was used to increase the stiffness of final thermosets.

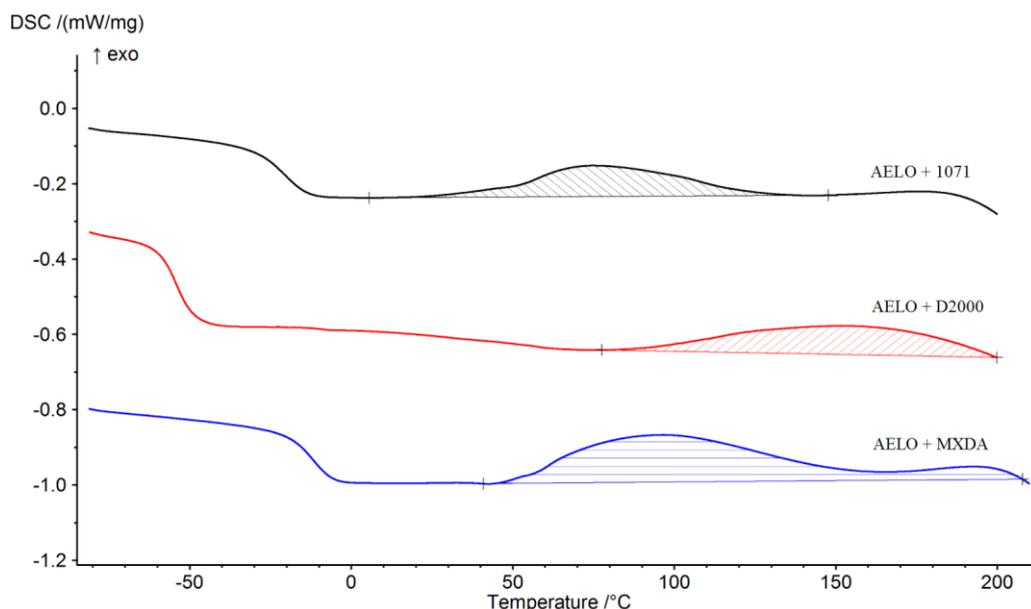


Figure 5. DSC curves of the curing of AELO with Priamine (black), D2000 (red) and MXDA (blue) (measured at 20 °C/min)

Priamine-based material presents a single enthalpy of reaction from room temperature (RT = 25 °C) to 150 °C. The couples AELO/MXDA and AELO/D2000 present enthalpies of reaction from 30 °C to 250 °C and from 75 °C to 250 °C respectively. The large enthalpy of AELO/MXDA can be separated into two reactions. The first one from 30 °C to 150 °C and the second one from 150 °C to 250 °C. Indeed this first enthalpy disappears after a first curing at room temperature for 24 h. Due to the large difference of reactivity of the primary amine compare to the formed secondary amine, this first enthalpy was attributed to the reaction of the primary amine whereas the second one was attributed to the reaction of the secondary amine. The lower steric hindrance of aliphatic amines strongly decreases the difference of reactivity of the both amines (I and II). Thus no second enthalpy are observed with Priamine. Total conversion at room temperature is obtained with Priamine but a post-cure at higher temperature is necessary for the reaction of the formed secondary amine of MXDA. DSC measurements of the mixture AELO/MXDA at each stage (before curing, after 24 h at room temperature and after post-curing) are shown in SI-Figure 12. These curves highlight the presence of two enthalpies of reaction and the necessity of a post-cure.

Only one enthalpy of reaction is also observed for the couple AELO/D2000. Indeed, due to the strong steric hindrance of the α -substituted amine of D2000, the kinetics of the attack of the primary amine was slowed. The two enthalpies are thus very close and observed as only one.

Due to the high reactivity of the Priamine 1071, the reaction was expected to have already started at the beginning of DSC measurements. $T_{g0_{th}}$ has been calculated and compared to $T_{g0_{exp}}$. Both values are equal and around $-20\text{ }^{\circ}\text{C}$. Therefore the reaction has not started and area of enthalpies can be compared. The couple AELO/MXDA exhibited the highest value ($\Delta_rH = 48\text{ J/g}$) against 22 J/g for AELO/1071 and 17 J/g for AELO/D2000. Values of Δ_rH are proportional to the amount of reactive functions per gram. MXDA is the shortest amine whereas D2000 is the longest which corresponds to the order of Δ_rH values.

As a potential secondary reaction, the homopolymerization of AELO was also studied. Pure AELO was heated at $150\text{ }^{\circ}\text{C}$ for 5 h in an oven and the chemical structure was monitored by FTIR analyses. No variation of the spectrum was observed. Furthermore, DSC analyses from $25\text{ }^{\circ}\text{C}$ to $250\text{ }^{\circ}\text{C}$ were performed on pure AELO but no enthalpy of reaction was observed. Therefore, the homopolymerization of AELO was not considered as a side-reaction toward aza-Michael reaction.

Thermosets syntheses

In order to synthesize thermoset materials AELO was mixed with different diamines without any catalyst nor solvent. Curing process was chosen owing to the previous DSC studies to complete reaction between acrylates and amines. Each diamine was mixed with AELO and mixtures were put in a silicone mold at room temperature for 24 h. Materials from less reactive amines were post cured at $150\text{ }^{\circ}\text{C}$ for 1 h for MXDA and at $100\text{ }^{\circ}\text{C}/2\text{ h}$ and $150\text{ }^{\circ}\text{C}/1\text{ h}$ for D2000 and D400 respectively to achieve the complete cross-linking.

Table 1. Structural characterizations of cured thermosets

Materials	Gel content (%)	Conversion (%)*
AELO + 1071	96	83
AELO + D400	91	62
AELO + D2000	94	65
AELO + MXDA	100	79

* Determined by FTIR

Gel content (Table 1) corresponds to the residual mass of materials after immersion in THF and drying. With values above 91%, no free species remain in the network and the cross-linking is complete for AELO-based materials.

The conversion of acrylate functions after curing with amines was measured by FTIR (Table 1). The disappearance of acrylate peaks at 1620 cm^{-1} was monitored and compared to the

C=O band at 1700 cm^{-1} as reference. FTIR spectra of thermosets are shown in SI-Figure 11. As previously observed with kinetics studies in DSC, Priamine and MXDA are the most reactive amines. They led to materials with the highest conversions. On the other hand, the methyl function in α -position of the PPG-based amines decreases their reactivity and the formed secondary amine is not very reactive. This high steric hindrance causes low values of conversion for PPO-based materials. This low conversions explain the lower values of gel content.

Thermal properties

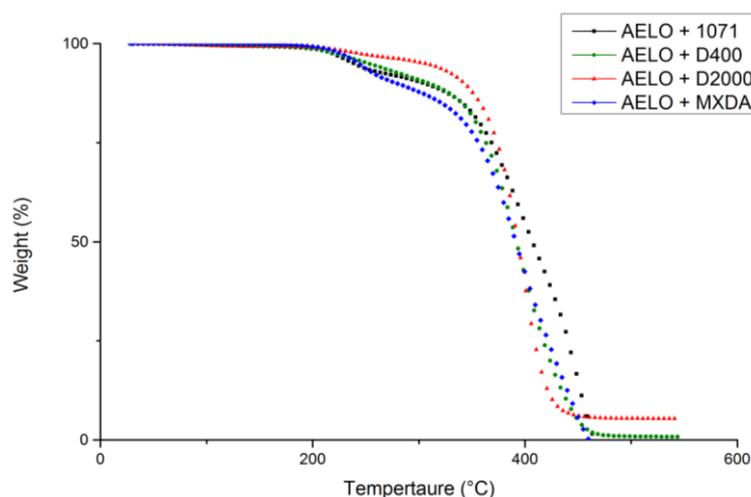


Figure 6. ATG curves of cured thermosets (black: AELO+1071; green: AELO+D400; red: AELO+D2000; blue: AELO+MXDA)

The thermal stability of thermosets was explored by TGA from $25\text{ }^{\circ}\text{C}$ (room temperature) to $550\text{ }^{\circ}\text{C}$ under inert atmosphere (N_2). ATG curves are shown in Figure 6 and the results are summarized in Table 2. The degradation temperatures of all materials are quite similar and around $240\text{ }^{\circ}\text{C}$. Two different degradation occurs. The first one around $300\text{ }^{\circ}\text{C}$ is assigned to the degradation of the ester functions. This can explain the slightly higher values of degradation ($T_{d5\%} = 305\text{ }^{\circ}\text{C}$) for D2000-based materials. Indeed, due to the high molar mass of D2000, its mass in the formulation is higher than AELO. Hence, for a same equivalent of material, AELO/D2000 presents the less content of ester functions. The first degradation is thus minor. Finally, due to the aliphatic structure of thermosets the residues at $550\text{ }^{\circ}\text{C}$ are very low.

Table 2. Physico-chemical properties of cured materials

Materials	$T_{d5\%}$ (°C)	Char yield (%)	T_g (°C)	T_a (°C)	E'_{glassy} (MPa)	E'_{rubbery} (MPa)	ν' (mol/m ³)
AELO + 1071	239	0	13	14	950	8.1	871
AELO + D400	252	0	-5	13	2300	8.8	946
AELO + D2000	305	5	-42	-31	2150	1.8	193
AELO + MXDA	243	0	31	41	1000	9.6	1032

Thermo-mechanical properties

The complete cross-linking was demonstrated by the absence of any enthalpy of reaction in the DSC measurements on cured materials. These analyses give also access to glass transition temperature (T_g) of each final materials. Results are summarized in Table 2 and curves are shown in SI-Figure 13. The T_g is linked to the mobility of the chains in the network. Material cured with D2000 present the lowest T_g value (-42 °C) due the length of the amine which is composed of around 33 units of propylene oxide (PO). With around 6 units of PO per diamine, D400-based material presents lower molecular weight between cross-linking nodes and thus lower mobility in the network and higher T_g (-5 °C). In comparison, Priamine 1071 has soft aliphatic chains and also a high functionality (≈ 2.2). Furthermore AELO/Priamine thermoset presents the highest conversion. A higher cross-linking density is thus expected and explains the higher T_g (13 °C). MXDA is the shortest amine with aromatic ring and led to highest degree of cross-linking, lowest mobility of the chains and conferred stiffness to the network. Therefore AELO/MXDA material exhibited the highest T_g (31 °C).

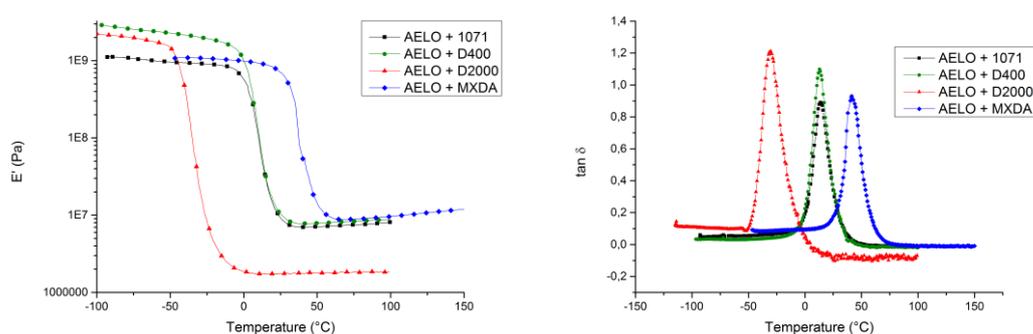


Figure 7. DMA measurements of thermosets (left: storage modulus (E'), right: $\tan \delta$), (black: AELO+1071; green: AELO+D400; red: AELO+D2000; blue: AELO+MXDA)

Thermo-dynamical properties of materials have been evaluated *via* dynamical mechanical analysis (DMA) and the results are summarized in Table 2. The values of storage modulus

(E') and $\tan \delta$ as function of the temperature are shown in Figure 7. The alpha-transition temperatures T_α have been measured at the maximum of the $\tan \delta$ for each material. According to the theory of rubber elasticity,[35] the molecular weight between the crosslinking-nodes of a cured network is proportional to its storage modulus in the rubbery region. Thus, the cross-linking density (ν') has been calculated on the rubbery domain at 100°C for each material. All the materials present a good homogeneity as shown by the narrow peaks of $\tan \delta$. T_α follow the same trend than T_g with slightly higher values and materials are ranked as follow: D2000 < D400 ≤ 1071 < MXDA. The low T_α , -31 °C for D2000 and 13 °C for D400 are partly explained by the soft structure of PPO. Furthermore, the lengths of D2000 and D400 cause a low cross-linking density with large spaces between the cross-linking nodes which is confirmed by the value of the cross-linking density ν' (respectively 193 mol/m³ and 946 mol/m³). These spacers bring mobility to the network and are therefore linked to the low T_α . The material cured with Priamine 1071 and the one with D400 present similar T_α (respectively 14 °C and 13°C) and ν' (respectively 871 and 946 mol/m³). Indeed, despite the long aliphatic and soft structure of Priamine 1071, this amine possesses a functionality of around 2.2 against 2 for D400. Higher conversions are also obtained with Priamine. Given their T_g values, highest properties are expected for AELO/Priamine thermoset. It is important to know that, due to the high reactivity of this couple, some bubbles could remain in the thermoset and be responsible of a reduction of the thermo-mechanical properties. Finally, due to the aromaticity and the short length of the amine, the material cured with MXDA presents the highest values of T_α (41 °C) and ν' (1032 mol/m³). The measure of the storage modulus (E') in the rubbery domain gives information on the stiffness of materials. The values of E' follow the same trend than T_g and T_α values. D2000-based material is the softest material (1.8 MPa) whereas MXDA-based material is the stiffest one (9.6 MPa). Along with T_α and ν' values, Priamine-based and D400-based materials have quite similar values (respectively 8.1 and 8.8 MPa).

CONCLUSIONS

Aza-Michael reaction was performed between acrylated linseed oil and various amines to afford novel biobased thermosets. The role of hydroxyl in vicinal position to acrylate functions was firstly studied by FTIR and DSC analyses on model molecules which allowed to highlight the strong activation of acrylates by hydroxyl groups. The use of such structure is an interesting way to overcome conversion and kinetic limits. The attack of the secondary amine on acrylate is thus accessible without the use of catalyst, solvent or high temperature conditions. Different amines were used to synthesize AELO-based thermosets. Kinetics of curing were compared by DSC and FTIR measurements. With fast reaction time, Priamine 1071 affords fully biobased materials after simple curing at room temperature. In order to decrease the gelation time and facilitate processing, D2000, D400 and MXDA were also studied as curing agents. The steric hindrance of these amines limits the attack of the secondary amine. The primary amine is also slowed down for D2000 and D400 and thermal activation is necessary. The thermal and thermo-dynamical properties of cured materials were finally discussed. The structure of amines strongly affects the rigidity of the network. Materials with a large range of T_g are obtained from soft (AELO+D2000) to stiff (AELO+MXDA).

REFERENCES

- [1] Galià, M., Montero de Espinosa, L., Ronda, J.C., Lligadas, G., Cádiz, V., Vegetable oil-based thermosetting polymers, *European Journal of Lipid Sciences and Technology*, 2010, 112, 87-96
- [2] Maisonneuve, L., Lebarbé, T., Grau, E., Cramail, H., Structure–properties relationship of fatty acid-based thermoplastics as synthetic polymer mimics, *Polymer Chemistry*, 2013, 4, 5472-5517
- [3] Dworakowska, S., Bogdal, D., Prociak, A., Microwave-Assisted Synthesis of Polyols from Rapeseed Oil and Properties of Flexible Polyurethane Foams, *Polymers* 2012, 4, 1462-1477
- [4] Lligadas, G., Ronda, J.C., Galià, M. and Cádiz, V., Renewable polymeric materials from vegetable oils: A perspective, *Mater. Today*, 2013, 16, 337–343.
- [5] Xia, Y. and Larock, R.C., Vegetable oil-based polymeric materials: Synthesis, properties, and applications, *Green Chem.*, 2010, 12, 1893–1909.
- [6] Zhang, C., Garrison, T.F., Madbouly, S.A., Kessler, M.R., *Prog. Polym. Sci.*, 2017, 71, 91–143.
- [7] Meier, M.A.R., Metzger, J.O., Schubert, U.S. *Chem. Soc. Rev.*, 2007, 36, 1788.
- [8] Sharma, V. and Kundu, P.P., Addition polymers from natural oils-A review, *Prog. Polym. Sci.*, 2006, 31, 983–1008.
- [9] Biermann, U., Friedt, W., Lang, S., Lühs, W., Machmüller, G., Metzger, J.O., Rüschen. Klaas, M.H., Schäfer, J., Schneider, M.P., New Syntheses with Oils and Fats as Renewable Raw Materials for the Chemical Industry, *Angew. Chemie Int. Ed.*, 2000, 39, 2206–2224.
- [10] Saurabh, T., Patnaik, M., Bhagst, S.L., Renge, V.C., Epoxidation of Vegetable Oils: a Review, *Int. J. Adv. Eng. Technol.*, 2011, 2, 459–501.
- [11] Danov, S.M., Kazantsev, O.A., Esipovich, A.L., Belousov A.S., Rogozhin, A.E., Kanakov, E.A., Recent advances in the field of selective epoxidation of vegetable oils and their derivatives: A review and perspective, *Catal. Sci. Technol.*, 2017, 7, 3659–3675.

- [12] Desroches, M., Caillol, S., Lapinte, V., Auvergne, R., Boutevin, B., Synthesis of biobased polyols by thiol-ene coupling from vegetable oils, *Macromolecules*, 2011, 44, 2489–2500.
- [13] Bähr, M. and Mülhaupt, R., Linseed and soybean oil-based polyurethanes prepared via the non-isocyanate route and catalytic carbon dioxide conversion, *Green Chem.*, 2012, 14, 483.
- [14] Robin, J.-J., Lapinte, V., Habas, J.P., Stemmelen, M., Caillol, S., Pessel, F., A fully biobased epoxy resin from vegetable oils. From the synthesis of the precursors by thiol-ene reaction to the study of the final material, *J. Polym. Sci. Part A Polym. Chem.*, 2011, 49, 2434–2444.
- [15] Lee, A. and Deng, Y., Green polyurethane from lignin and soybean oil through non-isocyanate reactions, *Eur. Polym. J.*, 2015, 63, 67–73.
- [16] Gurunathan, T. and Chung, J.S., Physicochemical properties of amino-silane-terminated vegetable oil-based waterborne polyurethane nanocomposites, *ACS Sustain. Chem. Eng.*, 2016, 4, 4645–4653.
- [17] Pelletier, H., Belgacem, N., Gandini, A., Acrylated vegetable oils as photocrosslinkable materials, *J. Appl. Polym. Sci.*, 2006, 99, 3218–3221.
- [18] Grishchuk, S. and Karger-Kocsis, J., Hybrid thermosets from vinyl ester resin and acrylated epoxidized soybean oil (AESO), *Express Polym. Lett.*, 2011, 5, 2–11.
- [19] Fu, L., Yang, L., Dai, C., Zhao, C., Ma, L., Thermal and mechanical properties of acrylated epoxidized-soybean oil-based thermosets, *J. Appl. Polym. Sci.*, 2010, 117, 2220–2225.
- [20] Akesson, D., Skrifvars, M., Walkenstrom, P., Preparation of thermoset composites from natural fibres and acrylate modified soybean oil resins, *J. Appl. Polym. Sci.*, 2009, 114, 2502–2508.
- [21] Black, M. and Rawlins, J.W., Thiol-ene UV-curable coatings using vegetable oil macromonomers, *Eur. Polym. J.*, 2009, 45, 1433–1441.
- [22] Mather, B.D., Viswanathan, K., Miller, K.M., Long, T.E., Michael addition reactions in macromolecular design for emerging technologies, *Prog. Polym. Sci.*, 2006, 31, 487–531.

- [23] Nair, D.P., Podgórski, M., Chatani, S., Gong, T., Xi, W., Fenoli, C.R., Bowman, C.N., The Thiol-Michael Addition Click Reaction: A Powerful and Widely Used Tool in Materials Chemistry, Bowman. *Chem. Mater.*, 2014, 26, 724–744.
- [24] Chatani, S., Wang, C., Podgórski, M., Bowman, C.N., Triple shape memory materials incorporating two distinct polymer networks formed by selective thiol-Michael addition reactions, *Macromolecules*, 2014, 47, 4949–4954.
- [25] Ding, X., Yang, C., Li, Y., Huang, Y., Hedrick, J.L., Yang, Y.Y., Liu, S.Q., Fan, W.M., Antimicrobial and Antifouling Hydrogels Formed In Situ from Polycarbonate and Poly(ethylene glycol) via Michael Addition, *Adv. Mater.*, 2012, 24, 6484–6489.
- [26] Li, Y. and Sun, X. S., Synthesis and characterization of acrylic polyols and polymers from soybean oils for pressure-sensitive adhesives, *RSC Adv.*, 2015, 5, 44009–44017.
- [27] Francucci, G., Cardona, F., Manthey, N.W., Cure kinetics of an acrylated epoxidized hemp oil-based bioresin system, *J. Appl. Polym. Sci.*, 2013, 128, 2030–2037.
- [28] Behera, D. and Banthia, A.K., Synthesis, characterization, and kinetics study of thermal decomposition of epoxidized soybean oil acrylate, *J. Appl. Polym. Sci.*, 2008, 109, 2583–2590.
- [29] Wuzella, G., Mahendran, A.R., Müller, U., Kandelbauer, A., Teischinger, A., Photocrosslinking of an Acrylated Epoxidized Linseed Oil: Kinetics and its Application for Optimized Wood Coatings, *J. Polym. Environ.*, 2012, 20, 1063–1074.
- [30] Salih, A.M., Bin Ahmad, M., Ibrahim, N.A., HjMohd Dahlan, K.Z., Tajau, R., Mahmood, M.H., Yunus, W.M.Z.W., Synthesis of radiation curable palm oil-based epoxy acrylate: NMR and FTIR spectroscopic investigations, *Molecules*, 2015, 20, 14191–14211.
- [31] Bonnaillie, L.M. and Wool, R.P., Thermosetting foam with a high bio-based content from acrylated epoxidized soybean oil and carbon dioxide, *J. Appl. Polym. Sci.*, 2007, 105, 1042–1052.
- [32] Wang, C., Ding, L., He, M., Wei, J., Li, J., Lu, R., Xie, H., Cheng, R., Facile one-step synthesis of bio-based AESO resins, *Eur. J. Lipid Sci. Technol.*, 2016, 118, 1463–1469.
- [33] Kasetaitė, S., De la Flor, S., Serra A., Ostrauskaitė, J., Effect of selected thiols on cross-linking of acrylated epoxidized soybean oil and properties of resulting polymers,

- Polymers (Basel)*, 2018, 10, 439.
- [34] Paramarta, A. and Webster, D.C., The exploration of Michael-addition reaction chemistry to create high performance, ambient cure thermoset coatings based on soybean oil, *Prog. Org. Coatings*, 2017, 108, 59–67.
- [35] Flory, P.J., Molecular Theory of Rubber Elasticity, *Polym. J.*, 1985, 17, 1–12.
- [36] Paramarta, A. and Webster, D.C., Highly Functional Acrylated Biobased Resin System for UV-Curable Coatings, *RADTECH Report*, 2013.
- [37] Lu, J. and Wool, R.P., Novel thermosetting resins for SMC applications from linseed oil. Synthesis, characterization, and properties, *J. Appl. Polym. Sci.*, 2006, 99, 2481–2488.
- [38] Wu, D., Liu, Y., He, C., Chung, T., Goh, S., Effects of Chemistries of Trifunctional Amines on Mechanisms of Michael Addition Polymerizations with Diacrylates, *Macromolecules*, 2004, 37, 6763–6770.
- [39] Sanui, K. and Ogata, N., The Catalytic Effect of Alcohol and Mercaptan on the Michael Reaction of Acrylates, *Bull. Chem. Soc. Jpn.*, 1967, 40, 1727–1727