



Article Application of Vegetable Oil-Based Monomers in the Synthesis of Acrylic Latexes via Emulsion Polymerization

Martin Kolář¹, Jana Machotová^{1,*}^D, Martin Hájek²^D, Jan Honzíček¹^D, Tomáš Hájek³^D and Štěpán Podzimek¹^D

- ¹ Institute of Chemistry and Technology of Macromolecular Materials, Faculty of Chemical Technology, University of Pardubice, 53210 Pardubice, Czech Republic
- ² Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice, 53210 Pardubice, Czech Republic
- ³ Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, 53210 Pardubice, Czech Republic
- * Correspondence: jana.machotova@upce.cz; Tel.: +420-466-037-194

Abstract: In this work, two bio-based raw materials, rapeseed oil and technical-grade oleic acid, were modified to yield acrylated monomers. Polymeric latexes designed for coating applications were synthesized using emulsion polymerization. Methyl methacrylate and butyl acrylate were copolymerized with various ratios of the acrylated bio-based monomers (0–20 wt.% in the monomer mixture). The polymerization with high monomer conversion and low coagulum content was successfully performed up to the content of 15 wt.% of the bio-based monomers, leading to long-term stable latexes. The asymmetric flow field flow fractionation coupled with a multi-angle light scattering detector was used to describe the molar mass distribution of the synthesized copolymers. Ultrahigh molar mass fractions were detected in copolymers comprising the bio-based monomers due to the presence of multi-acrylated bio-based ingredients originating from linoleic and linolenic fatty acids. This phenomenon became more pronounced for the rapeseed oil-originated monomer. The prepared latexes comprising copolymerized bio-based monomers showed comparable or even better coating performance in terms of gloss and water resistance in comparison with the reference acrylic coating, which makes the acrylated vegetable oil-based monomers attractive for the manufacturing of sustainable water-borne materials in the coating industry.

Keywords: rapeseed oil; oleic acid; acrylic latex; emulsion polymerization; molar mass; AF4; coating

1. Introduction

Synthetic latexes are a versatile and eco-friendly class of polymer materials with increasing global production. They are widely used in architectural paints, adhesives, sealants, and textile, or paper coatings. Latexes are produced via emulsion polymerization, a process of radical polymerization involving the emulsification of unsaturated monomers in water using a surfactant, followed by the initiation reaction with a water-soluble initiator [1,2]. Typical monomers used in emulsion polymerization are petroleum-based raw materials such as esters of acrylic and methacrylic acid, styrene, or vinyl acetate. In recent years, an interest in utilizing sustainable and renewable resources of eco-friendly and cost-effective materials has increased due to growing environmental concerns within the scientific and industrial communities [3–8], which also affects the area of emulsion polymerization [9].

Vegetable oils (triglycerides of higher fatty acids), which are produced from plants, seem to be an option for the replacement for fossil resources because of their availability, chemical versatility, structural variety, biodegradability, and most importantly, sustainability. Vegetable oils such as linseed [10], sunflower [11], soybean [12,13], castor [14], and rapeseed oil [15] have ordinarily been used for the synthesis of polymers. These plant oils



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). vary especially by the profile of bonded higher fatty acids, i.e., the carbon chain length (most often 18 carbons) and the level of unsaturation [16–18]. The present research is focused on the utilization of rapeseed oil as the most widespread plant oil in Europe (63% of the oilseeds production in 2017) [19]. It consists of about 56 % oleic acid, 26% linoleic acid, 10% linolenic acid, and 6% saturated acids [20,21].

Unfortunately, the double bonds present in higher fatty acids are usually not reactive enough to perform effectively in free radical polymerization. Therefore, vegetable oils cannot be easily converted to polymers without introducing more reactive functionalities, such as vinyl, epoxy, or hydroxyl groups, into their molecules [22,23]. Different pathways for modifying oils into useful monomers have been published, including epoxidation [24–26], acrylation [27–31], and hydroxymethylation [32]. The modified vegetable oils have been used to produce various polymers designed for different applications, e.g., acrylic adhesives [33], polyurethane composites [34], and alkyd coatings [35,36].

Incorporating monomers derived from vegetable oils via emulsion polymerization remains quite a challenge because of the hydrophobic nature of their triglyceride molecules. Their low solubility in water limits transport and incorporation into resulting polymer particles [37,38]. Nevertheless, some successful attempts have been reported [39]. Vinyl monomers derived from different vegetable oils (soybean, olive, sunflower, and linseed oil) were copolymerized with methyl methacrylate (MMA), styrene, and vinyl acetate. It was found that the presence of the bio-based monomers (up to 35 wt.% in the monomer mixture) caused a decrease in both the glass transition temperature and molar mass of resulting polymers, the latter effect being attributed to the degradative chain transfer to the bio-based monomer [40–42]. On the contrary, crosslinking occurring during the copolymerization of MMA with higher proportions (above 40 wt.%) of a castor oil-based vinyl monomer was evidenced in the case of polymers prepared by mini-emulsion polymerization [43].

This work is focused on the synthesis of film-forming vegetable oil-based polymer latexes via emulsion polymerization. Two bio-based monomers composed of acrylated methyl esters of higher fatty acids were synthesized from rapeseed oil (RO) and technicalgrade oleic acid (OA), respectively. The effect of the type and content of the bio-based monomer was investigated in terms of monomer conversion, colloidal stability, chemical structure, and glass transition temperature of resulting copolymers. Special attention was paid to the study of the molar mass distribution of acrylic copolymers, determined using asymmetric flow field flow fractionation (AF4) coupled with a multi-angle light scattering (MALS) detector. Basic coating properties, such as gloss, adhesion, and water resistance, were also evaluated to estimate the performance of the synthesized bio-based latexes in the protection of various substrates, such as wood, steel, and masonry.

2. Materials and Methods

2.1. Materials

The following reactants were used for the synthesis of the bio-based monomers: rapeseed oil (RO, PREOL, Lovosice, Czech Republic), technical-grade oleic acid (OA, 70%, Penta Chemicals, Prague, Czech Republic, CAS:112-80-1), hydrogen peroxide (30%, technical grade, Lach-Ner, Brno, Czech Republic, CAS: 7722-84-1), methanol (Penta Chemicals, Prague, Czech Republic, CAS: 67-56-1), potassium hydroxide (Lach-Ner, Brno, Czech Republic, CAS: 1310-58-3), diethyl ether (Lach-Ner, Brno, Czech Republic, CAS: 60-29-7), sulfuric acid (Lach-Ner, Brno, Czech Republic, CAS: 7664-93-9), potassium carbonate (Lach-Ner, Brno, Czech Republic, CAS: 584-08-7), formic acid (Lach-Ner, Brno, Czech Republic, CAS: 64-18-6), acrylic acid (AA, Sigma-Aldrich, Schnelldorf, Germany, CAS: 79-10-7), hydroquinone (Lach-Ner, Brno, Czech Republic, CAS: 3444-17-5), ethyl acetate (Lach-Ner. Brno, Czech Republic, CAS: 141-78-6), and sodium carbonate (Lach-Ner, Brno, Czech Republic, CAS: 497-19-8). All the chemicals were used as received.

In all emulsion polymerization reactions methyl methacrylate (MMA, CAS: 80-62-6), butyl acrylate (BA, CAS:141-32-2), and methacrylic acid (MAA, CAS: 79-41-4) were used as

monomers (Sigma-Aldrich, Schnelldorf, Germany), Disponil FES 993 (sodium salt of fatty alcohol polyglycol ether sulfate, BASF, Prague, Czech Republic) as surfactant, ammonium persulfate (Lach-Ner, Brno, Czech Republic, CAS: 7727-54-0) as initiator, and 2-amino-2-methyl-1-propanol (AMP 95, Sigma-Aldrich, Schnelldorf, Germany, CAS: 124-68-5) as neutralizing agent. All the chemicals were used as received without further purification.

2.2. Synthesis and Characterization of Bio-Based Monomers

In the first step, the methyl ester of RO (ME_RO) and methyl ester of OA (ME_OA) were obtained by transesterification of RO and esterification of OA. The transesterification was carried out with 420 g of RO, 92 g of methanol, and 3.7 g of potassium hydroxide as a catalyst. The reaction temperature was 60 °C and the reaction time was 90 min. The esterification was carried out with 220 g of OA, 152 g of methanol, and 287 g of diethyl ether as cosolvent. The mixture was heated to 42 °C and 28 g of sulfuric acid as a catalyst was added. After 4 h, the esterification was stopped by neutralization of the catalyst with potassium carbonate. Then, diethyl ether and methanol were removed by distillation. Formed ME_RO and ME_OA were separated from glycerol or water in a separatory funnel.

The second step involved the epoxidation of the double bonds in ME_RO and ME_OA resulting in an epoxidized methyl ester of RO (EME_RO) and epoxidized methyl ester of OA (EME_OA), respectively. The epoxidation reaction was carried out in a batch reactor with 420 g of the respective methyl ester (ME_RO, ME_OA), 345 g of hydrogen peroxide, 60.3 g of formic acid as a catalyst, and 3.2 g of sulfuric acid as an additional catalyst. The mixture of the given methyl ester (ME_RO, ME_OA), formic acid, and sulfuric acid was cooled to 8–10 °C and then hydrogen peroxide was gradually added over 30 min at a stirring speed of 300 rpm. The reaction mixture was heated to 60 °C for 3 h. The reaction was stopped by the addition of potassium carbonate until the pH of the epoxide phase was neutral. After that, the aqueous phase was removed by decantation in a separatory funnel.

The last step involved the acrylation of EME_RO and EME_OA by AA, resulting in acrylated methyl ester of RO (AME_RO) and acrylated methyl ester of OA (AME_OA), respectively. The laboratory procedure involved mixing 50 g of EME_RO and EME_OE, respectively, 17 g of AA, 0.15 g of hydroquinone, and 0.5 g of chromium (III) 2-ethyl hexanoate in a three-necked round-bottom flask, equipped with a reflux condenser, magnetic stirrer, and a thermometer. The solution was vigorously stirred and kept at 100 °C using an oil bath for 6 h. After that, the excess amount of AA was neutralized using a saturated solution of sodium bicarbonate. An extraction was then performed, using a mixture of ethyl acetate and water (1:1 w/w). The separated organic layer was desiccated with sodium carbonate, and ethyl acetate was evaporated from the product with constant stirring at room temperature (RT).

The prepared methyl esters, epoxidized methyl esters, and acrylated methyl esters of RO and OA were further characterized in terms of their chemical structure, the content of non-epoxidized and non-acrylated methyl esters of different higher fatty acids, and the iodine value. The chemical structure of the compounds was investigated using infrared (IR) vibration spectroscopy on a Nicolet iS50 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) equipped with a build-in diamond ATR (attenuated total reflection) crystal in the region of $4000-400 \text{ cm}^{-1}$ (data spacing = 0.5 cm⁻¹). Concurrently, Raman spectra were acquired by a Nicolet iS50 spectrometer with an FT-Raman module (Nd:YAG excitation laser $\lambda = 1064$ nm, power = 0.5 W, data spacing = 1 cm⁻¹) in the region of 4000–200 cm⁻¹. The methyl esters of different higher fatty acids was analyzed by gas chromatography coupled with mass spectroscopy (GC-MS). The Agilent 7890B/5977A Series GC/MSD (Agilent Technologies, Waldbronn, Germany) equipped with an autosampler (Agilent 7693) and operating in the electron ionization (EI) mode was used for monitoring and identification of compounds. The electron energy of EI was 70 eV, the source temperature was 300 °C, the quadrupole temperature was 150 °C and the transfer line temperature was 300 °C. MS data were acquired over a mass range of 50–500 at a rate of 6 scan/s. A TRACETM TR-FAME capillary column, 60 m \times 0.25 mm I.D., film thickness

0.25 µm (Thermo Fisher Scientific, Waltham, MA, USA) under gradient conditions was used for separation of all compounds in the sample. Helium at a flow rate of 1 mL/min was used as the carrier gas with the following oven temperature program: 70 °C held for 3.5 min, the gradient of 90 °C/min to 160 °C held for 2 min, the gradient of 5 °C/min to 200 °C held to 1 min, the gradient of 2 °C/min to 240 °C held to 50 min. The amount of $0.5 \,\mu\text{L}$ sample was injected to GC under split mode injection with a 1:50 split ratio at 250 °C. The measurements were carried out two times. Samples were prepared as follows: 0.25 g of a tested material was weighed and dissolved in 3 g of acetonitrile. Then the solution was diluted five times with acetonitrile. C17:0 methyl ester (≥99.0%, Merck KGaA, Darmstadt, Germany) was used as the internal standard. The area of the peaks (A) and thus the representation of the individually detected compounds were related to the internal standard (AIS). The iodine value, which is a measure of the unsaturation of an organic compound, was determined using the Hanuš method [44]. The method consists of adding the excess of iodine monobromide (that reacts with double bonds in the unsaturated compound), followed by the treatment with potassium iodide and the determination of liberated iodine by titration with sodium thiosulfate.

2.3. Synthesis and Characterization of Latexes

Two series of latexes were prepared using the technique of semi-continuous nonseeded emulsion polymerization. The latex copolymers were synthesized starting from an initial composition of standard acrylic monomers (denoted as REF) on one hand and different mixtures of the bio-based monomers (AME_RO, AME_OA) and acrylic monomers, on the other hand, as can be seen in Table 1. The latex samples were labeled as X_y, where X represents the bio-based raw material type (RO or OA), and y is the percentage content of the respective bio-based monomer in the monomer mixture. The MMA/BA ratio of 21/28 (*w/w*) was maintained in all monomer compositions.

Sample Name	Bio-Based Monomer Content (wt.%)	Monomer (g)				
		MMA	BA	MAA	AME_RO	AME_OA
REF	0	21.00	28.00	1	-	-
RO_5	5	19.93	26.57	1	2.5	-
RO_10	10	18.86	25.14	1	5.0	-
RO_15	15	17.79	23.71	1	7.5	-
RO_20	20	16.72	22.28	1	10.0	-
OA_5	5	19.93	26.57	1	-	2.5
OA_10	10	18.86	25.14	1	-	5.0
OA_15	15	17.75	23.71	1	-	7.5
OA_20	20	16.72	22.28	1	-	10.0

Table 1. Names of latex samples and the respective amounts of monomers in the monomer mixture.

The latexes were produced in a 700 mL glass reactor under an inert atmosphere (nitrogen) at 85 °C. The reactor charge consisting of 16.25 g of demineralized water, 0.125 g of Disponil FES 993, and 0.175 g of ammonium persulfate was heated to the polymerization temperature. Then the monomer emulsion consisting of 50 g of the monomer mixture (Table 1), 57.5 g of demineralized water, 3.7 g of Disponil FES 993, and 0.35 g of ammonium persulfate was dosed into the reactor at the feed rate of about 2 mL/min. After that, the reaction mixture was allowed to polymerize for 2 h. Each latex sample obtained from the corresponding initial monomer composition was synthesized 3 times.

After the synthesis, the latexes were filtered, and the coagulum was collected. The coagulum content and monomer conversion were determined by the gravimetric method and were calculated according to Equations (1) and (2) [45].

coagulum content (%) =
$$\frac{m_C}{\frac{m_2 \times m_L}{m_1} + m_C} \times 100$$
 (1)

monomer conversion (%) =
$$\frac{\frac{m_2 \times m_T}{m_1} - (m_I + m_S)}{m_M} \times 100$$
 (2)

where m_1 is the weight of a liquid latex portion; m_2 is the weight of the latex portion dried to a constant weight at 110 °C; m_C is the weight of the dried coagulum; m_L is the weight of the total filtered latex; m_T is the total weight of all the materials put in the reaction flask; m_I is the weight of the initiator; m_S is the weight of the surfactant (active matter); m_M is the weight of the total monomers.

The pH of latexes was then adjusted to 8.5 with AMP 95 (50% aqueous solution). The storage stability of latexes was evaluated according to changes in the average particle size and the zeta potential after storing the latexes at 40 °C for 60 days. The average particle sizes and the zeta potential of the latex particles dispersed in the water phase were detected by dynamic light scattering (DLS) using a Litesizer 500 instrument (Anton Paar GmbH, Graz, Austria). The concentration of a solid polymer in the water phase was 0.01 wt.% and the measurements were conducted at 25 °C.

The molar mass distribution of latex copolymers was determined by asymmetric flow field flow fractionation (AF4) coupled with a multi-angle light scattering (MALS) detector. The employed AF4-MALS instrumental set-up consisted of an Agilent 1260 Infinity II chromatograph (Agilent, Santa Clara, CA, USA) with a quaternary pump and an autosampler with a Wyatt Technology AF4 system Eclipse coupled with a MALS photometer DAWN and an Optilab refractive index (RI) detector. The system was completed with an online viscometer ViscoStar for a more detailed characterization of the molecular structure of some of the analyzed samples. All detectors and software were acquired from Wyatt Technology (Santa Barbara, CA, USA). The separation was achieved with a long channel of 350 µm thickness and regenerated cellulose membrane of 10 kDa cut-off. The carrier was tetrahydrofuran (THF). A linear cross flow gradient from 2.5 mL/min to 0.1 mL/min over 15 min followed by 0.1 mL/min for 20 min and zero cross flow for 10 min was used for the separation with the channel flow and detector flow of 1 mL/min and 0.3 mL/min, respectively. Samples were prepared in THF at the concentration of ≈ 2.5 mg/mL, left to dissolve for at least 48 h, filtered with 0.45 μ m filter, and injected in the amount of 100 μ L. ASTRA 8 was used for data collection and processing, VISION was used for the operation of the Eclipse (both Wyatt Technology).

2.4. Preparation and Characterization of Coatings

Liquid latexes were applied onto glass panels using a blade applicator. The thickness of the wet coatings was 120 µm. There were no coalescing agents used. After curing at RT $(23 \pm 1 \text{ °C})$ and $40 \pm 5\%$ of relative humidity for 1 week, the resulting films were evaluated in terms of their gloss, water contact angle (WCA), adhesion, glass transition temperature (T_g) , and chemical composition. The gloss of coatings, cast on glass panels coated with black matte paint (RAL 9005), was measured by means of a micro-TRI-gloss μ instrument (BYK-Gardner, Geretsried, Germany) using a gloss-measuring geometry at 60°. WCAs were examined using an optical tensiometer Attension Theta (Biolion Scientific, Espoo, Finland). A water drop of 1 µL was always applied and the steady-state WCA value was subtracted at the time of 10 s. Ten measurements were performed for each coating sample at RT and $40 \pm 5\%$ RH. The adhesion (expressed as pull strength) of coatings to a glass substrate was evaluated in accordance with ISO 4624 using an Elcometer 510 Automatic Adhesion Tester (Elcometer Instruments, UK). T_{g} was determined by differential scanning calorimetry (DSC) on a Pyris 1 DSC instrument (Perkin-Elmer, Waltham, MA, USA). The measurements were performed under an inert atmosphere (nitrogen) atmosphere at a heating rate of 10 °C/min from –50 °C to 120 °C (Tg was determined from the second heating curve). Fourier transform infrared (FT-IR) spectroscopy was used to detect the incorporation of vegetable oil-based monomers into latex copolymers. Infrared spectra of the samples were recorded on a Nicolet iS50 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) using a build-in diamond ATR (attenuated total reflection) crystal in the region of 4000–400 cm⁻¹ (data spacing = 0.5 cm^{-1}).

3. Results and Discussion

3.1. Characterization of Bio-Based Monomers

Based on the procedures described in the relevant literature [27,46–49], two bio-based monomers composed of acrylated methyl esters of higher fatty acids were synthesized by a three-step procedure from RO and OA (technical-grade oleic acid), respectively (Figure S1). The methyl ester of RO (ME_RO) and methyl ester of OA (ME_OA) were obtained by RO transesterification and OA esterification. In the case of the synthesis of esters of higher fatty acids from vegetable oils, transesterification has been shown to be particularly effective [49]. This procedure results in saving two reaction steps compared to saponification of vegetable oil followed by acidification and esterification of free higher fatty acids [27]. The epoxidation of double bonds in ME_RO and ME_OA resulting in the epoxidized methyl ester of RO (EME_RO) and epoxidized methyl ester of OA (EME_OA) was further performed. Finally, the acrylation of EME_RO and EME_OA using AA led to the acrylated methyl ester of RO (AME_RO) and acrylated methyl ester of OA (AME_OA), respectively. The acrylation reaction consisted of the oxirane ring opening leading to the incorporation of the acryloyl group together with the formation of a hydroxyl group. The scheme of AME_OA synthesis is shown in Figure 1.



Figure 1. Schematic illustration of AME_OA synthesis from oleic acid.

Vibration spectroscopy was used to follow the process of the synthesis of the biobased monomers (Figures 2 and 3). ME_RO and ME_OA showed IR absorption bands of medium intensity at 2924 and 2854 cm⁻¹ that were assigned to antisymmetric ($\nu_a(C-H)$) and symmetric C–H stretching ($\nu_s(C-H)$) of methylene groups of fatty acid tails, respectively. The presence of methyl groups was associated with the absorption bands of weak intensity at 2957 cm⁻¹ ($\nu_a(C-H)$) and 2875 cm⁻¹ ($\nu_s(C-H)$). C=O stretching of the ester moiety appeared in the IR spectrum as a band of very strong intensity at 1737 cm⁻¹. In the Raman spectrum, it was observed as a band on the medium intensity at 1740 cm⁻¹. Unsaturation of the fatty acid tails is evident from the characteristic C–H stretching mode of the cisC=C-H moiety appearing in the IR spectrum at 3007 cm⁻¹ and in the Raman spectrum at 3011 cm⁻¹. Stretching of the C=C double bond is observed in the Raman spectrum as a band of medium intensity at 1656 cm⁻¹. Note that this vibration mode is silent in the IR spectrum, as the dipole moment of the symmetrically substituted C=C bond does not change during stretching.



Figure 2. Vibration spectra of ME_RO (black), EME_RO (blue), and AME_RO (red).



Figure 3. Vibration spectra of ME_OA (black), EME_OA (blue), and AME_OA (red).

Epoxidation of ME RO and ME OA resulted in a decrease in the intensity of the C=C stretching band in EME_OA and EME_RO intermediate products. Comparing the integral intensity C=C stretching band for the corresponding methyl esters and epoxidized methyl esters revealed ~83% and 94% conversion of the epoxidation process for ME_RO and ME_OA, respectively. High conversion is also apparent from the disappearance of the CH stretching mode of the cis-C=C–H moiety and the appearance of the IR band at 825 cm⁻¹ assigned to the out-of-plane CH bending of the epoxy group. Successful acrylation of EME_RO and EME_OA was proved by the appearance of new bands in the region of C=C stretching (IR: 1637 cm⁻¹, Raman: 1638 cm⁻¹) and C=O stretching modes (IR: 1724 cm⁻¹, Raman: 1725 cm⁻¹) in the case of both AME_RO and AME_OA. Lower wavenumbers of the vibration modes are attributed to conjugation between the C=O and C=C double bond of the acrylate. The vinyl group of the acrylate gives CH stretching band at 3038 cm⁻¹. Opening of the epoxide ring was further revealed by the appearance of a broad IR band at 3505 cm⁻¹ assigned to the formed OH group and the disappearance of epoxide group CH bending δ (C–H) at 826 cm⁻¹. It is noteworthy that residual C=C double bonds from ME_RO and ME_OA are evidenced even in their acrylated counterparts.

The content of methyl esters of different higher fatty acids (i.e., molecules without oxirane rings and attached acryloyl groups) in the intermediate products (ME_RO, ME_OA,

EME_RO, and EME_OA) and the final bio-based monomers (AME_RO and AME_OA) was determined by the GC-MS method (Table 2). It was found that the content of methyl esters of higher fatty acids in ME_RO and ME_OA intermediate products was different. ME_OA contained more than 75% of methyl ester of oleic acid (C18:1) and 14% of methyl ester of linoleic acid (C18:2), and 7% of methyl ester of palmitic acid (C16:0). The concentration of methyl ester of C18:1 in ME_RO was lower (57%) than in ME_OA, whereas the concentration of methyl ester of C18:2 was almost twice as high (26%), and the sample contained also about 6% of methyl ester of linolenic acid (C18:3). A decrease in the concentration of all unsaturated higher fatty acid-based fractions was observed after epoxidation in the EME_RO and EME_OA intermediate products. The content of the most represented fraction of methyl ester of C18:1 decreased to about 10–11% in both cases (approximately six times for EME_RO and seven times for EME_OA), which means that this fraction was not completely converted to epoxides. For EME_RO, the content of methyl ester of C18:2 and methyl ester of C18:3 decreased 22 and 62 times, respectively. For EME_OA, a decrease in the content of methyl ester of C18:2 was similar, i.e., a higher level of fatty acid unsaturation into the ME_OA intermediate product means a higher conversion to epoxides. The acrylation reaction was the last step to obtain the acrylated bio-based monomers. Analysis of AME_RO and AME_OA final products showed an additional slight decrease in the concentration of non-epoxidized and non-acrylated methyl esters of higher fatty acids (C16:0 and C18:0), which is only a consequence of the increase in molar mass of unsaturated higher fatty acid-based fractions due to the modifying reactions (epoxidation, acrylation) resulting in "mass dilution" of the analyzed mixture.

Fatty Acid Type	Content of Methyl Ester of Higher Fatty Acid (wt.%)						
	ME_RO	EME_RO	AME_RO	ME_OA	EME_OA	AME_OA	
C16:0	5.7	4.5	3.6	7.2	6.7	5.8	
C18:0	2.3	1.4	1.2	2.1	1.9	1.6	
C18:1	57.4	10.4	8.3	76.2	11.2	8.8	
C18:2	26.4	1.2	0.9	13.9	0.6	0.2	
C18:3	6.2	0.1	0.1	_*	-*	_*	
C20:1	0.9	0.1	0.1	0.4	_*	_*	
others	1.2	0.6	0.4	0.1	0.1	0.1	
Σ	100.0	18.3	14.5	100.0	20.5	16.6	

Table 2. Representation of non-epoxidized and non-acrylated methyl esters of different higher fatty acids in intermediate products, and final bio-based monomers originated from RO and OA.

* Not detected.

The prepared bio-based monomers including the intermediate products were also characterized by iodine value (Table 3), which reflects the level of unsaturation. It was confirmed that epoxidation of ME_RO and ME_OA resulted in a drop in the iodine value, however, some double bonds were found to be still intact, which is in a good accordance with GC-MS results discussed above (consider data for the C18:1 fraction). Acrylation then caused an increase in the iodine value due to the presence of C=C double bonds in the attached acryloyl groups. When comparing RO and OA-based products, higher iodine values were always detected in the case of all RO-based products. This finding correlates again with the GC-MS results that revealed a higher representation of C18:2 and C18:3 fractions in the ME_RO intermediate product. Consequently, a higher extent of acrylation was found in AME_RO than in AME_OA.

Table 3. Iodine values for intermediate products, and final bio-based monomers originated from RO and OA.

Sample	ME_RO	EME_RO	AME_RO	ME_OA	EME_OA	AME_OA
Iodine value (g I ₂ /100 g)	108.2 ± 2.5	17.7 ± 1.4	54.1 ± 1.3	85.1 ± 2.1	7.5 ± 0.8	49.4 ± 2.2

3.2. Characterization of Latexes

Acrylic latexes were synthesized via semi-continuous non-seeded emulsion polymerization (Figure S1). This technique is unique in ensuring the so-called monomer-starved conditions during free-radical polymerization, which results in the achievement of high immediate conversion of monomers and a relatively homogeneous chemical composition of statistical copolymers [50]. The characteristic properties of the prepared latexes are listed in Table 4. It was found for latexes modified by the bio-based monomers (AME_RO and AME_OA) that the coagulum formed during the emulsion polymerization increased slightly up to the bio-based monomer content of 15 wt.%, whereas the synthesis of latex samples RO_20 and OA_20 (modified by 20 wt.% of the respective bio-based monomer) was accompanied by an intense coagulum formation. This phenomenon was probably caused by the presence of multi-acrylated and non-acrylated fractions in the bio-based monomers. The incorporation of the multi-acrylated oil-based ingredients (originated especially from linoleic and linolenic fatty acid-based fractions) with a crosslinking potential could result in polymer particles prone to aggregation, as has been observed in the case of polymerizations with higher amounts of multi-vinyl crosslinking monomers, such as allyl methacrylate [51,52]. On the contrary, the non-acrylated oil-based ingredients (represented by methyl esters of saturated higher fatty acids, in particular the methyl ester of palmitic acid, and by the non-acrylated methyl esters of unsaturated higher fatty acids, especially the methyl ester of oleic acid), incapable to undergo polymerization, behaved in the polymerization system as sticky impurities that are usually responsible for an increased tendency to aggregation [53]. Nevertheless, the tests further revealed that the incorporation of both types of bio-based monomers did not significantly affect monomer conversion, particle size, and zeta potential latex products. Zeta potential values indicate sufficient colloidal stability of all synthesized latexes [54]. As for storage stability, all latexes, regardless of the type and amount of the bio-based monomer, provided long-term stability under storage at elevated temperatures.

			Particle Size (nm)		Zeta Potential (mV)	
Sample	Coagulum (%)	Conversion (%)	Before Storing	After Storing	Before Storing	After Storing
REF	1.7 ± 1.1	94.3 ± 1.0	102.1 ± 0.9	104.0 ± 1.6	-42.2 ± 0.2	-38.5 ± 1.1
RO_5	3.3 ± 1.4	95.0 ± 0.7	100.2 ± 1.3	102.3 ± 1.1	-44.4 ± 0.9	-41.5 ± 0.6
RO_10	3.8 ± 0.4	93.1 ± 1.0	108.2 ± 1.3	111.4 ± 1.0	-44.8 ± 0.3	-42.3 ± 0.8
RO_15	5.3 ± 0.4	93.9 ± 1.2	102.5 ± 1.0	106.8 ± 0.8	-40.3 ± 0.6	-41.7 ± 1.0
RO_20	21.3 ± 4.6	95.4 ± 1.9	96.3 ± 0.4	101.5 ± 0.9	-40.3 ± 0.8	-39.6 ± 0.4
OA_5	4.9 ± 1.0	95.6 ± 0.8	105.0 ± 1.6	106.9 ± 1.3	-40.3 ± 1.7	-41.2 ± 0.9
OA_10	5.3 ± 1.2	94.7 ± 0.9	101.1 ± 1.7	105.1 ± 0.7	-46.1 ± 0.5	-40.2 ± 0.6
OA_15	7.2 ± 2.5	96.7 ± 1.8	95.2 ± 1.2	99.9 ± 1.5	-42.6 ± 1.0	-41.0 ± 1.3
OA_20	18.9 ± 6.9	95.5 ± 1.2	90.3 ± 1.0	96.7 ± 0.6	-44.0 ± 1.0	-39.0 ± 0.8

Table 4. Properties of latexes and results of their storage stability testing (storing at 40 °C for 60 days).

3.3. Molar Mass Determination of Latex Copolymers

The molar mass distribution of latex copolymers was determined by AF4-MALS which has proven to be an efficient method capable of describing the molar mass distribution and molecular structure of acrylic latex copolymers [55–57]. The molar mass versus retention time plots of the copolymers derived from the REF and RO_20/OA_20 samples (modified by 20 wt.% of the respective bio-based monomers) are comparatively shown in Figure 4. The RI fractograms of the modified copolymers show two baseline-separated peaks. The peak at lower retention times can be assigned to soluble macromolecules (in THF). The peak starting at the retention time of about 40 min resembles the peak found on the fractograms of acrylic polymers modified by the tetrafunctional ethylene glycol dimethacrylate [56]. These ultra-high molar mass species are highly branched polymer chains and crosslinked swollen nanogels.



Figure 4. Molar mass (blue) versus retention time plots overlaid on RI fractograms (black) of reference latex copolymer (**a**) and copolymers modified with 20 wt.% of AME_OA (**b**), and 20 wt.% AME_RO (**c**).

The molar mass distribution curves of the prepared copolymers are depicted in Figure 5. The data revealed a shift of the molar mass distribution towards the high molar masses in the case of copolymerizing bio-based monomers, which can be attributed to the copolymerization of multi-acrylated crosslinking ingredients in the bio-based monomers. This effect was more pronounced for the RO-based samples, which correlates well with GC-MS results (Table 2) that revealed a higher content of C18:2 and C18:3 fractions in ME_RO monomer giving the possibility of two and three polymerizable acryloyl groups, respectively. Note that the presence of tetra and six functional monomers may lead to the formation of branched ultra-high molar mass fractions during the emulsion polymerization. It was further shown that the content of ultra-high molar mass species increased with an increasing amount of copolymerized bio-based monomers. Similarly, this phenomenon was more distinct for the copolymers modified by the AME_RO monomer.



Figure 5. Cumulative molar mass distribution curves of latex copolymers modified with AME_RO (a) and AME_OA (b): reference copolymer (black), 5 wt.% (red), 10 wt.% (orange), 15 wt.% (green), and 20 wt.% (blue) of the respective bio-based monomer.

The measured values of the number-average $(\overline{M_n})$, the weight-average $(\overline{M_w})$ and the z-average $(\overline{M_{wz}})$ molar masses are listed in Table 5. The values of $\overline{M_n}$, which reflects the lower molar mass region of the distribution, were independent of composition and there was also no difference between the modified and reference copolymers. The higher molar mass moments of modified copolymers were markedly increased due to the branching caused by the multi-functional fractions in the bio-based monomers. The distribution curves also show an increasing amount of ultra-high molar mass fractions eluting beyond the retention time of \approx 40 min. Extraordinarily high values of $\overline{M_w}$ and $\overline{M_z}$ for copolymers modified by 10 wt.% of AME_RO are probably due to small amounts of molecules with a molar mass over $\approx 10^8$ g/mol.

Table 5. Molar mass averages and dispersity of latex copolymers modified by AME_RO and AME_OA. Results are averages from three measurements.

Sample	$\overline{M_n}^*$ (10 ³ g/mol)	$\overline{M_w}^*$ (10 ⁶ g/mol)	$\overline{M_z}^*$ (10 ⁶ g/mol)	$\overline{M_w}/\overline{M_n}$
REF	170	6.1	18	36
RO_5	140	31.4	83	224
RO_10	120	119.7	3360	998
RO_15	160	81.4	133	509
RO_20	170	67.0	112	394
OA_5	150	9.6	31	64
OA_10	140	17.3	48	124
OA_15	150	19.7	49	131
OA_20	130	24.5	50	188

* The measurement uncertainty was <10%.

The difference between the copolymers modified by AME_RO and AME_OA is further evident from the Mark–Houwink plots shown in Figure 6. The plots of modified copolymers overlay in the region of lower molar masses up to $\approx 10^6$ g/mol, whereas the ultra-high molar mass fractions are markedly more compact in the case of the AME_RO modified copolymer. Basically, the markedly different molecular structure of modified copolymers compared to that that of copolymers associated with the REF sample is additional evidence that the bio-based monomers were really incorporated into the final polymer chains.



Figure 6. Mark–Houwink plots of reference copolymer (black) and copolymers modified with 20 wt.% of AME_OA (blue), and 20 wt.% of AME_RO (red).

3.4. Characterization of Coatings

The incorporation of the bio-based monomers into the acrylic backbone was evidenced by a detailed analysis of the IR spectra (Figure 7). Region of CH stretching modes shows well-resolved C–H stretching bands of methyl and methylene groups. The reference polymer coating of unmodified acrylic copolymer showed two CH stretching bands of medium intensity at 2956 cm⁻¹ and 2874 cm⁻¹ assigned to antisymmetric and symmetric vibration modes of methyl groups, respectively. The weak absorption bands located at 2931 and 2855 cm⁻¹ and assigned to the CH stretching vibrations of the methylene groups increased in intensity with increased content of copolymerized bio-based monomers, as fatty acid tails of bio-based monomers raise the content of the methylene group considerably. The schematic chemical composition of acrylic polymer coating comprising copolymerized bio-based monomers is depicted in Figure 8.



Figure 7. Detailed IR spectra of polymer coatings modified with AME_RO (**a**) and AME_OA (**b**): reference copolymer (black), 5 wt.% (red), 10 wt.% (orange), 15 wt.% (green), and 20 wt.% (blue) of the respective bio-based monomer.

The coating properties of films cast on glass substrates were also evaluated (Table 6, Figure S2). Regardless of the type and content of the incorporated bio-based monomers, all the prepared coating films were transparent, exhibited high gloss, and had similar adhesion to a glass substrate. The latter effect can be attributed to the presence of hydroxyl groups of oleic side chains (Figure 8), weakening their water-repellent nature. On the contrary, the modification with the bio-based monomers affected the surface properties

of coatings, the higher the bio-based monomer content, the more increased the water resistance (represented by a decrease in wettability measured using WCA). This effect, demonstrating the water-repellent character of the copolymerized bio-based monomers, was found to be more pronounced in the case of introducing the AME_OA monomer. It was further found that the application of the bio-based monomers resulted in a significant decrease in T_g . This phenomenon became more pronounced with the increasing content of the introduced bio-based monomer, regardless of its type. The plasticizing effect, which is in good accordance with relevant literature data [37,40,47], is related to the presence of flexible side chains (provided by the bio-based monomers) in the acrylic polymer backbone (Figure 8).



Figure 8. Illustration of the chemical structure of latex polymer composed of copolymerized MMA (*n*), BA (*o*), MAA (*p*), and AME_OA (*q*).

Table 6. Coating properties.

Sample	Gloss 60 $^{\circ}$ (GU)	Pull Strength (MPa)	WCA (°)	Tg (°C)
REF	83.5 ± 0.1	3.3 ± 0.3	64.9 ± 1.5	1.3 ± 0.3
RO_5	83.8 ± 0.2	3.4 ± 0.2	66.6 ± 4.0	-2.7 ± 0.4
RO_10	83.7 ± 0.1	3.2 ± 0.2	72.6 ± 2.3	-5.3 ± 0.4
RO_15	84.2 ± 0.1	3.1 ± 0.3	70.6 ± 3.6	-8.2 ± 0.3
RO_20	83.7 ± 0.2	3.1 ± 0.2	66.7 ± 1.2	-12.4 ± 1.0
OA_5	83.5 ± 0.2	3.2 ± 0.3	67.7 ± 1.4	-2.6 ± 0.2
OA_10	83.1 ± 0.3	3.2 ± 0.4	70.2 ± 0.6	-5.7 ± 0.6
OA_15	83.4 ± 0.1	3.2 ± 0.2	73.3 ± 7.3	-7.5 ± 0.3
OA_20	84.1 ± 0.1	3.1 ± 0.2	76.2 ± 0.7	-10.8 ± 0.6

4. Conclusions

Two types of bio-based monomers composed of acrylated methyl esters of higher fatty acids were synthesized from rapeseed oil and technical-grade oleic acid. The biobased monomers were used to partially replace common acrylic monomers during the synthesis of polymer latexes designed for coating applications. It was shown that emulsion polymerizations exhibiting high monomer conversion and low coagulum content could be performed up to the content of 15 wt.% of the bio-based monomers. It was also evidenced that both types of bio-based monomers successfully copolymerized with standard acrylic monomers, which resulted in polymers comprising fractions with ultra-high molar mass and branched topology. The reason is the presence of multi-acrylated bio-based ingredients originating from linoleic and linolenic fatty acids. This effect increased with the increasing amount of the bio-based monomers and was more pronounced in the case of the rapeseed oil-based monomer. The prepared latexes modified with the bio-based monomers showed comparable or even better coating performance in terms of gloss, adhesion, and water resistance in comparison with the reference acrylic coating. The application of the biobased monomers also provided the coatings with a plasticizing effect, which makes the bio-based monomers attractive for the industrial production of renewable water-borne lacquers and paint binders. These materials can be used as adequate substitutes for traditional petroleum-based latex products designed for diverse coating applications, such as decorative or protective finishes of wooden, metal, and architectural surfaces.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/coatings13020262/s1, Figure S1: Illustration of the preparation process and appearance of bio-based intermediate prod-ucts, bio-based acrylated monomers and resulting polymer latexes; Figure S2: Component weight plot for the properties of liquid latexes, latex copolymers, and final coatings modified with AME_RO (a) and AME_OA (b).

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