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ORIGINAL PAPER

Synthesis and Characterization of Allyl Fatty Acid Derivatives as Reactive Coalescing Agents for Latexes

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Abstract This work evaluated the use of allyl fatty acid esters derived from vegetable oil (palmitic acid, soybean and sunflower oils) as reactive coalescing agents in a waterborne latex system. Allyl fatty acid derivatives (AFAD) from vegetable oils were synthesized by two different processes. The synthesis was monitored by IR-spectroscopy and the final product characterized by FT-IR, GC–MS, ^{1}H and ^{13}C NMR. The presence of conjugated double bonds in the aliphatic chain was confirmed, which is a determinant for the proposed autoxidative latexes drying mechanism. Each of the AFAD were subsequently added to a standard acrylic emulsion, in order to study its potential as reactive coalescing agent. The minimum film-forming temperature (MFT), glass transition temperature (T_g), drying time and rubbing resistance to solvents were evaluated. The results showed that, when added to water-borne acrylic resins, an AFAD acts as a non-volatile plasticizer capable of autoxidative crosslinking with itself.

Keywords Vegetable oils · Water-borne acrylic resins · Reactive coalescing agent · Oxidative cure

Introduction

Oils can be classified according to their ability to dry into a solid film. Drying oils can form a film at ambient temperatures, semi-drying oils need to be heated, and non-drying oils do not form a film. An increasing number of double bonds in the aliphatic chain leads to increasing drying rates, due to an autoxidation mechanism. The drying rate of oils can be further increased when conjugated double bonds are present in the alkyl chain [1].

Vegetable oils such as castor, linseed and sunflower oil can be easily transformed into acids with a long hydrocarbon chain. These are unsaturated acids containing at least one double bond, which allows for oxidative curing to occur when exposed to atmospheric oxygen. The oxygen attack causes double bond rearrangement and hydroperoxide formation [2]. This process occurs in commercial alkyd resins that, in addition to exhibiting physical drying–solvent evaporation, also undergo chemical drying–crosslinking due to autoxidation. Appropriate catalysts, often called driers, are added to increase the chemical drying rates [3, 4].

Several studies can be found on the functionalization of unsaturated vegetable oils by addition of acrylic, vinylic and styrenic groups, usually involving an esterification reaction [5, 6]. The purpose is often to incorporate these products into waterborne resins as co-monomers or homopolymers, therefore creating emulsion polymers containing internally plasticizing and crosslinking components [7–9]. Their use helps reduce the need for volatile co-solvents as coalescing agents, thus reducing volatile organic emissions from commercial waterborne coatings or adhesives.

These same derivatives can be used non-polymerized, as reactive coalescing agents with high boiling points [10, 11]. The reaction occurs upon drying via oxidation of

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the unsaturated double bonds. The type of bonds (conjugated or non-conjugated) affects the reaction mechanism significantly. When non-conjugated double bonds are present, the radicals formed recombine to form dimers. In conjugated fatty acids, a chain addition mechanism takes place, leading to more effective crosslinking [12, 13].

Studies on synthesis and polymerization of allyl esters of fatty acids have been known for several decades. Homopolymerization yields a low degree of polymerization products [14]. However, reasonably high conversions were reported for copolymerization with vinyl chloride, while copolymerization with styrene and methyl methacrylate does not occur to an appreciable extent [15, 16]. More recently, use of a monounsaturated allyl fatty acid derivative has been reported as a reactive diluent for solvent-based vinyl ester and polyester resins [17].

In the present work, allyl fatty acid derivatives (AFAD), derived from renewable resources (soybean and sunflower oils), were synthesized and their applicability as reactive coalescing agents for acrylic waterborne resins was evaluated. Different synthesis strategies were considered. A possible approach is the one-step esterification of a fatty acid with the allylic alcohol. However, in order to insure high conversion, a significant excess of alcohol and high temperatures must be used. The latter may lead to a decrease in the number of double bonds in the product. The other possibility is the two-step esterification via intermediate formation of highly reactive acyl chloride. This allows high conversions with shorter reaction times and moderate temperatures. Oil transesterification is a well-known process, with well-determined molar ratios, reaction times and temperatures [18, 19]. Therefore, AFAD synthesis was also attempted by this process.

Experimental

Materials

Sunflower oil derived conjugated fatty acids (CFA), soybean oil and a commercial acrylic polymer emulsion (product specification states that free residual monomer is less than 300 ppm) used in this study were kindly supplied by Resiquímica-Resinas Químicas, S.A. (Mem Martins, Portugal). Allylic alcohol, phosphorus trichloride and palmitic acid were purchased from Fluka; petroleum benzine from Merck; anhydrous magnesium sulfate ($MgSO_4$) and anhydrous calcium chloride ($CaCl_2$) from Panreac; deuterated chloroform ($CDCl_3$, 99.8 % D) from Sigma-Aldrich. All chemicals were used as received. The drying catalyst (3 % cobalt, 3 % barium and 5 % zirconium) was kindly supplied by CIN–Corporação Industrial do Norte (Maia, Portugal).

Characterization Methods

Infrared (IR) spectra were recorded with an ABB-Bomen spectrometer, the neat samples being placed in a sodium chloride cell. Each spectrum was an average of 32 scans taken with 4 cm^{-1} resolutions in the 4,000–650 cm^{-1} range.

^{1}H-NMR and ^{13}C-NMR spectra were acquired on a Bruker Avance 300 spectrometer operating at a frequencies of 300 and 75 MHz, respectively, using deuterated chloroform as solvent. Chemical shifts were reported in parts per million (ppm, δ) and referenced to $CDCl_3$.

Gas chromatography-flame ionization detection (GC-FID) was performed with a Chrompack CP-9001 coupled with a FID system and equipped with a CP-SiL 88 Column (50 m × 0.25 mm). Helium was used as the carrier gas at an internal pressure of 110 kPa. The following operating conditions were used: injector temperature was set at 250 °C while the detector temperature was set at 270 °C; the initial temperature of the column 140 °C, was maintained for 5 min, and was subsequently increased to 220 °C at 10 °C min^{-1}. The results are expressed in relative percentage of each fatty acid, calculated by internal normalization of the chromatographic peak area. Fatty acid identification was made by comparing the relative retention times of fatty acid methyl esters (FAME) peaks with standards. A Supelco (Bellefonte, PA) mixture of 37 FAME (standard 47885-U) was used.

Gas chromatography–mass spectroscopy (GC–MS) was performed with a 6890 Agilent-Little Falls equipped with an electronically controlled split/splitless injection port interfaced to a single quadrupole inert mass selective detector 5973 N-Agilent with an electron impact ionization chamber. GC separation was performed on a DB-5MS J&W capillary column (30 m × 0.25 mm ID., 0.25 μm film thickness). Helium was used as the carrier gas with a constant flow of 1 ml min^{-1}. The injection was made in split mode (40:1) at 250 °C. The oven temperature program was as follows: initial temperature 80° C for 1 min; ramped to 250 °C at 5 °C min^{-1}, then heated to 300 °C at 3 °C min^{-1} for 13 min. The MS transfer line temperature was held at 280 °C. The mass spectrometric parameters were set as follows: electron impact ionization with 70 eV energy; ion source temperature 230 °C, and MS quadrupole temperature 150 °C. The MS system was routinely set in full scan mode. An Agilent Chemstation was used for data collection/processing and GC–MS control.

Glass transition temperatures (T_g) were measured using a differential scanning calorimeter Setaram DSC 131 equipped with liquid nitrogen cooling. About 20 mg of liquid mixture were placed in DSC aluminium crucibles and placed in a desiccator to dry. The T_g was measured for increasing drying times, on different samples. The thermograms were recorded up to 100 °C, at a heating rate of 10 °C min^{-1}, under N_2 flow. The T_g values presented are an average for at least three films.

The minimum film-forming temperature (MFT) was determined according to standard procedure ISO 2115: 1996-Plastics-Polymer dispersions-Determination of white point temperature and minimum film-forming temperature.

Drying times of acrylic resins mixtures at 22 °C were determined by applying 100-μm wet thickness films on 10 × 15 cm glass plates and measuring the time until the surface was dry to the touch. The drying times presented are an average of at least three films.

A rubbing resistance test was conducted to evaluate the number of cycles (double rubs) to film failure. Rubbing was performed manually with a cotton piece previously wet with either xylene or acetone, along a 5-cm length of film.

AFAD Synthesis

AFAD from a Saturated Fatty Acid (Palmitic Acid) by Two Step Esterification

Palmitic acid (3.0 g, 12 mmol) was placed in a three-necked round-bottom flask, equipped with magnetic stirrer, thermometer, nitrogen bubbling and water condenser. The liquid was heated to 55 °C. Phosphorus trichloride (1.0 g, 8.0 mmol) was added dropwise, for 1 h. The reaction product was fatty acid acyl chloride, as confirmed by FT-IR. The mixture was cooled to 10 °C and allylic alcohol (0.7 g, 12 mmol) was added dropwise for 1 h. The esterification product consists of AFAD from palmitic acid (allyl palmitate). Both reactions were monitored via FT-IR. The reaction mixture was purified by liquid extraction in a separating funnel, and washed with petroleum benzine and distilled water, until a neutral pH was achieved. The organic layer was dried overnight with anhydrous magnesium sulfate and filtered. Finally the solvent was removed under a vacuum and the product obtained was characterized by FT-IR, NMR, GC-FID and GC–MS. The yield obtained was 78 %. *Palmitic acid*: **IR** (cm^{-1}): between 3,400 and 2,400 (OH stretching), 2,920 and 2,855 cm^{-1} (saturated $[(CH_2)_n]$ stretching), 1,700 (C=O stretching), 1,465 and 1,378 (CH_2, CH_3 bending), 1,295, 1,230 (C–O, stretching), 942, 726 (CH_2, rocking). **^{1}H NMR** ($CDCl_3$): δ in ppm (J in Hz) = 0.88 (t, J = 7.2, 3H, CH_3, H_{-16}), 1.20–1.50 (m, 24H, aliphatic CH_2, H_{-4}–H_{-15}), 1.65 (m, 2H, $–CH_2–CH_2–C(=O)$-, H_{-3}), 2.35 (t, J = 7.2, 2H, $–CH_2$-$C(=O)$–, H_{-2}), 11.30 (brs, OH). **^{13}C NMR** ($CDCl_3$): δ in ppm = 14.14 ($–CH_3$, C_{-16}), 22.76 (C_{-15}), 24.80 (C_{-3}), 28.0–30.0 [$(CH_2)_n$, C_{-4}–C_{-13}], 32.05 (C_{-14}), 34.23 (C_{-2}), 180.58 ($–C(=O)–$, C_{-1}). **GC-EIMS (FAME)–**: *m/z* (rel int %) = 270 (M^+, 9), 241 (3), 239 (5), 227 (15), 213 (2), 199 (5), 185 (4), 171 (4), 157 (2), 143 (16), 129 (9), 115 (3), 101 (8), 87 (74), 74 (100), 55 (24). *Allyl palmitate*: **IR** (cm^{-1}): 3,088 (unsaturated CH_2 anti-symmetric stretching), 3,005 (CH unsaturated stretching), 2,920 and 2,855 (saturated $[(CH_2)_n]$ stretching), 1,740 (C=O stretching), 1,650 (C=C stretching), 1,465 and 1,378 (CH_2, CH_3 bending), 1,173 (C–O, stretching), 990 and 930 ($CH=CH_2$, out-of-plane deformation), 723 (CH_2, rocking). **^{1}H NMR** ($CDCl_3$): δ in ppm (J in Hz) = 0.88 (t, J = 7.2, 3H, CH_3, H_{-16}), 1.20–1.40 (m, 24H, aliphatic CH_2, H_{-4}–H_{-15}), 1.64 (m, 2H, $–CH_2–CH_2–C(=O)–$, H_{-3}), 2.34 (t, J = 7.2, 2H, $–CH_2–C(=O)–$, H_{-2}), 4.58 (ddt, 2H, J = 10.5, 1.6 and 1.6 Hz, $–OCH_2–CH=CH_2$, $H_{-1'}$), 5.23 (ddt, 1H, J = 10.5, 1.6 and 1.6 Hz, $CH_2=CH–$, $H_{-3'}$), 5.33 (ddt, 1H, J = 17.2, 1.6 and 1.6 Hz, $CH_2=CH–$, $H_{-3'}$) and 5.93 (ddt, 1H, J = 17.2, 10.5 and 5.7 Hz, $CH_2=CH–$, $H_{-2'}$). **^{13}C NMR** ($CDCl_3$): δ in ppm = 14.06 ($–CH_3$, C_{-16}), 22.65 (C_{-15}), 24.91 (C_{-3}), 29.0–30.0 [$(CH_2)_n$, C_{-4}–C_{-13}], 31.89 (C_{-14}), 34.92 (C_{-2}), 64.85 ($CH_2=CH–CH_2O–$, $C_{-1'}$), 117.96 ($CH_2=CH–$, $C_{-3'}$), 132.31 ($CH_2=CH–$, $C_{-2'}$) and 173.45 ($–C(=O)–$, C_{-1}). **GC-EIMS**: *m/z* (rel int %) = 296 (M^+, 4), 281 (6), 267 (6), 253 (17), 239 (38), 225 (6), 211 (8), 197 (4), 181 (2), 169 (21), 157 (9), 139 (8), 125 (11), 113 (94), 100 (100), 85 (45), 71 (53), 57 (77).

AFAD from Conjugated Fatty Acids by Two Step Esterification

The conjugated fatty acids (CFA) mixture composition is shown in Table 1. CFA were charged into a three-necked round-bottom flask (150 g, 0.536 mol), equipped with magnetic stirrer, thermometer, nitrogen bubbling and water condenser, and was heated to 60 °C. Phosphorus trichloride (21 g, 0.18 mol) was added dropwise for 1 h. The reaction product was cooled to 35 °C and allylic alcohol (102 g, 1.75 mol) was added dropwise for 45 min. The reaction was continued for 1 h to guarantee maximum production of AFAD (yield 76 %). Both reactions were monitored via FT-IR. The purification process was made following the procedure described above. *Conjugated Fatty Acids* (*CFA*): **IR** (cm^{-1}): between 3,400 and 2,400 (OH stretching), 3,009 (CH unsaturated stretching), 2,920 and 2,855 cm^{-1} (saturated $[(CH_2)_n]$ stretching), 1,711 (C=O stretching), 1,654 (C=C stretching), 1,465 and 1,378 (CH_2, CH_3 bending), 1,173 (C–O stretching), 982 and 946 (($CH=CH_2$, out-of-plane deformation), 723 (CH_2, rocking). **^{1}H NMR** (C18:2 Δ^{9Z-11E}, $CDCl_3$): δ in ppm (J in Hz) = 0.90 (t, J = 7.2, 3H, CH_3, H_{-18}), 1.20–1.50 (m, 16H, aliphatic CH_2, H_{-4}–H_{-7} and H_{-14}–H_{-17}), 1.65 (m, 2H, $–CH_2–CH_2–C(=O)–$, H_{-3}), 2.00–2.30 (m, 4H, H_{-8}, H_{-13}), 2.32 (t, J = 7.2, 2H, $–CH_2–C(=O)–$, H_{-2}), 5.4 (dt, J = 11.0 and 7.0 Hz, H_{-9}), 5.7 (dt, J = 15.0 and 7.0 Hz, H_{-12}), 6.0 (t, J = 11.0 Hz, H_{-10}) and 6.4 (dd, J = 15.0 and 11.0 Hz, H_{-11}), 11,30 (brs, OH).

^{13}C NMR (C18:2 Δ^{9Z-11E}, $CDCl_3$): δ in ppm = 13.91 (–CH_3, C_{-18}], 22.56 (C_{-17}), 24.50 (C_{-3}), 25.0–33.0 [$(CH_2)_n$, C_{-4}–C_{-8}, C_{-13}–C_{-15}], 31.821(C_{-16}), 33.93 (C_{-2}), 125.00–135.00 (C_{-9}–C_{-12}), 180.21 (–C(=O)–, C_{-1}). **GC-EIMS** (C18:2 conjugated-**FAME)–***m/z* (rel int %) = 294 (M^+, 31), 263 (12), 220 (6), 178 (6), 164 (9), 150 (13), 136 (11), 123 (13), 109 (25), 95 (51), 81 (73), 67 (100), 55 (39). *Allyl fatty acid derivatives from CFA*: **IR** (cm^{-1}): 3,088 (unsaturated CH_2 anti-symmetric stretching), 3,009 (CH unsaturated stretching), 2,920 and 2,855 cm^{-1} (saturated [$(CH_2)_n$] stretching), 1,741 (C=O stretching), 1,650 (C=C stretching), 1,465 and 1,378 (CH_2, CH_3 bending), 1,173 cm^{-1} (C–O, stretching), 989 and 930 ($CH=CH_2$, out-of-plane deformation), 723 (CH_2, rocking). **^{1}H NMR** ($CDCl_3$): δ in ppm (*J* in Hz) = 0.85 (t, *J* = 7.2, 3H, CH_3, H_{-18}), 1.20–1.40 (m, 16H, aliphatic CH_2, H_{-4}–H_{-7} and H_{-14}–H_{-17}), 1.58 (m, 2H, –$\underline{CH_2}$–CH_2–C(=O)–, H_{-3}), 2.26 (t, *J* = 7.2, 2H, –CH_2–C(=O)–, H_{-2}), 4.50 (ddt, 2H, *J* = 10.5, 1.6 and 1.6 Hz, –OCH_2–$CH=CH_2$, $H_{-1'}$), 5.14 (ddt, 1H, *J* = 10.5, 1.6 and 1.6 Hz, CH_2=CH–, $H_{-3'}$), 5.23 (ddt, 1H, J = 17.2, 1.6 and 1.6 Hz, CH_2=CH–, $H_{-3'}$), 5.28 (dt, *J* = 11.0 and 7.0 Hz, H_{-9}), 5.45 (dt, *J* = 15.0 and 7.0 Hz, H_{-12}), 5.60 (t, *J* = 11.0 Hz, H_{-10}), 5.85 (ddt, 1H, *J* = 17.2, 10.5 and 5.7 Hz, CH_2=CH–, $H_{-2'}$), and 5.95 (dd, *J* = 15.0 and 11.0 Hz, H_{-11}). **^{13}C NMR** ($CDCl_3$): δ in ppm = 13.67 (–CH_3, C_{-18}), 22.32 (C_{-17}), 24.54 (C_{-3}), 29.00–30.00 [$(CH_2)_n$, C_{-4}–C_{-8}, C_{-13}–C_{-15}], 31.92 (C_{-16}), 33.71 (C_{-2}), 64.34 (CH_2=CH–CH_2O–, $C_{-1'}$), 125.00–135.00 (C_{-9}–C_{-12}), 117.25 (CH_2=CH–, $C_{-3'}$), 132.11 (CH_2=CH–, $C_{-2'}$), 172.52 (–C(=O)–, C_{-1}). **GC-EIMS** (C18:2, conjugated): 320 (M^+, 4), 263 (6), 235 (38), 220 (6), 165 (21), 111 (94), 100 (100), 85 (42), 83 (45), 71 (53), 69 (55), 57 (77).

Table 1 Composition (%) of fatty acid methyl esters (FAME) and allyl fatty acid derivatives (AFAD) from conjugated fatty acids (CFA)

Relative (%)	FAME from CFA	AFAD from CFA
C14:0	0.11	–
C16:0	7.16	6.62
C16:1	0.12	0.13
C18:0	3.63	3.42
C18:1	27.52	25.36
C18:2	10.95	11.67
C20:0	0.25	0.24
C20:1	0.31	0.31
CLAs	47.66	50.31
C22:0	0.72	0.53
C22:1	0.26	0.27
C24:0	0.11	0.09
C24:1	0.28	0.12
Others	0.92	0.93

AFAD from Soybean Oil by Transesterification

Soybean oil (10 g, 11 mmol) was placed into a three-necked round-bottom flask, equipped with a water condenser, thermometer, and magnetic stirrer, and was heated to 65 °C. The mixture of allylic alcohol (4.0 g, 69 mmol) and catalyst, NaOH (0.2 mg, 10 mmol), was added dropwise for over 1 h [20]. After complete addition the reaction proceeded for 2 h under vigorous stirring. At the end, products were left to settle to ensure separation of the two phases. The purification process was made following the procedure described above. *Soybean oil*: IR (cm^{-1}): 3,009 (CH unsaturated stretching), 2,926 and 2,855 cm^{-1} (saturated [$(CH_2)_n$] stretching), 1,746 (C=O stretching), 1,654 (C=C stretching), 1,461 and 1,374 (CH_2, CH_3 bending), 1,237, 1,164 cm^{-1} (C–O, stretching), 1,100, 969 and 914 ($CH=CH_2$, out-of-plane deformation), 722 (CH_2, rocking). *Allyl fatty acid derivatives from soybean oil:* **IR** (cm^{-1}): 3,085 (unsaturated CH_2 anti-symmetric stretching), 3,009 (CH unsaturated stretching), 2,927 and 2,856 cm^{-1} (saturated [$(CH_2)_n$] stretching), 1,741 (CH_2=CH–CH_2–OCO–), 1,651 (C=C stretching), 1,461 and 1,377 (CH_2, CH_3 bending), 1,238, 1,171 (C–O, stretching), 990 and 928 ($CH=CH_2$, out-of-plane deformation), 722 (CH_2, rocking).

Results and Discussion

Synthesis Monitoring

The AFAD from palmitic acid (allyl palmitate) (*n* = 14) were prepared by a two-step esterification (Fig. 1) and characterized by IR-spectroscopy and nuclear magnetic resonance (NMR). Since it is derived from a saturated fatty acid it is not expected to exhibit autoxidative properties and was used as a control reference.

The disappearance of the broad band corresponding to OH stretching (3,400–2,400 cm^{-1}) in carboxylic acid groups and the shift of carbonyl band of palmitic acid from 1,700 to 1,740 cm^{-1}, corresponding to the formation of the ester carbonyl group (C=O stretching vibration) in AFAD are shown in Fig. 2e, f. To calculate the percentage of each carbonyl group present during the reactions, several samples were withdrawn at 10 min intervals and analysed by IR spectroscopy. Carbonyl groups were quantified based on peak height. The disappearance of the carbonyl group band from CFA (1,711 cm^{-1}), the formation of a new carbonyl band of fatty acid acyl chloride (first step) (1,804 cm^{-1}) and its disappearance to be replaced by AFAD carbonyl group (second step) (1,741 cm^{-1}) are shown in Fig. 3a. The decrease in CFA during the first 40 min and the formation of the reaction product, namely fatty acid acyl chloride are shown in Fig. 3b. After the disappearance of

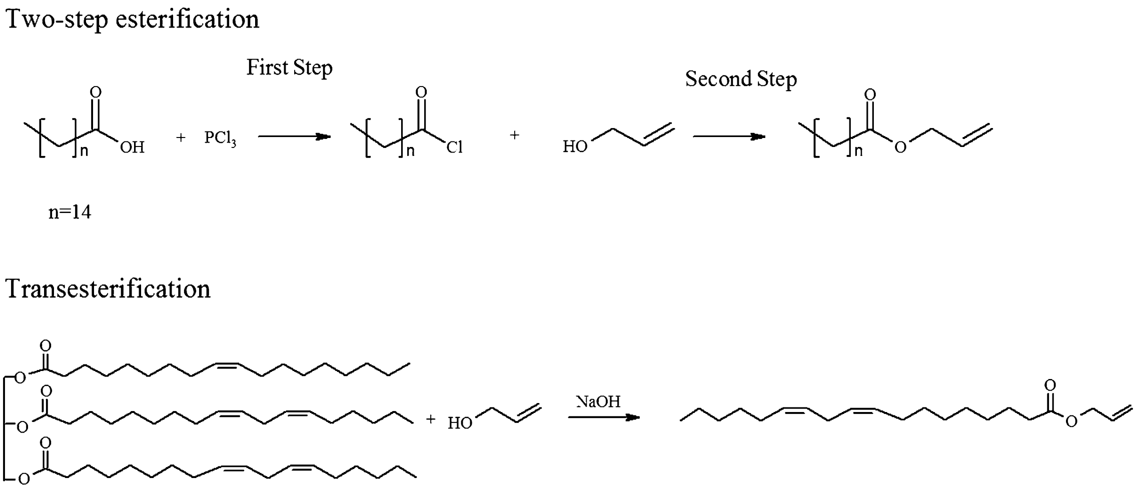

Fig. 1 General scheme of the reactions involved in the AFAD synthesis process. 255 × 191 mm (150 × 150 DPI)

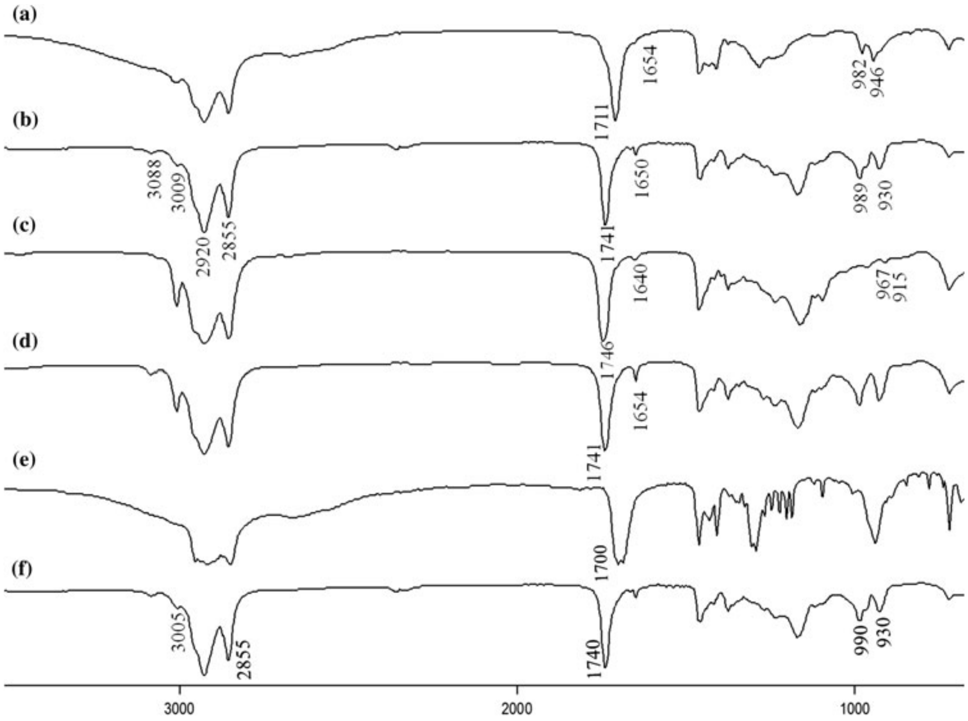

Fig. 2 FTIR spectra of **a** conjugated fatty acids (CFA), **b** AFAD from CFA, **c** soybean oil, **d** AFAD from soybean oil, **e** palmitic acid and **f** allyl palmitate. 261 × 191 mm (150 × 150 DPI)

CFA (45 min) the reaction was stopped and cooled, and then allylic alcohol was added (second step). The AFAD amount increases along the first 45 min of the second step (until $t = 90$ min) and then stabilizes. Acyl chloride absorption was detected only at the beginning of the second step, since its slow addition avoided accumulation in the reaction medium.

FT-IR Characterization

The characterization of the synthesized AFAD structure can be done by comparing the IR spectra of the raw materials and the products obtained (Fig. 2). All IR spectra are similar, showing the presence of two bands below 3,000 namely at 2,920 and 2,855 cm^{-1} (saturated $[(\text{CH}_2)_n]$ stretching) and one band above 3,000, specifically at 3,009 cm^{-1} (CH unsaturated stretching).

In all synthesis, the appearance of two bands at 930 and 989 cm^{-1}, corresponding to allylic group ($\text{CH}=\text{CH}_2$, out-of-plane deformation), was observed for the reaction products. In addition, the presence of this allylic group causes the appearance at 3,088 cm^{-1} of one band (unsaturated CH_2 anti-symmetric stretching) and an increased

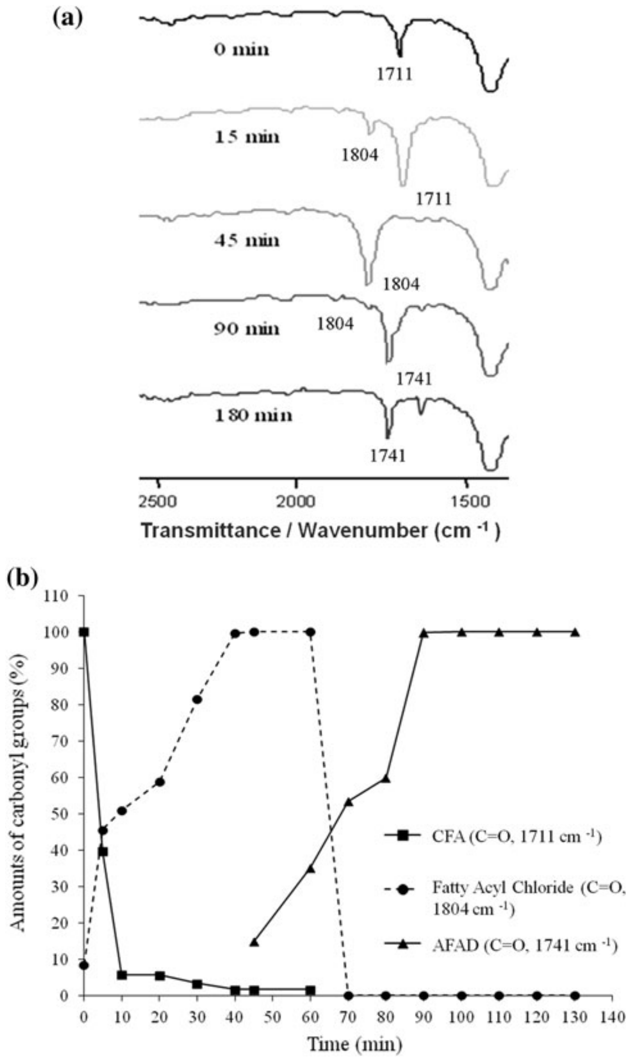

Fig. 3 AFAD reactions monitored by **a** infrared and **b** evolution of absorptions bands during the formation of fatty acyl chloride (first step) and AFAD (second step). 276 × 310 mm (150 × 150 DPI)

intensity of bands at 1,650 cm^{-1} (C=C stretching) and at 3,009 cm $^{-1}$ (unsaturated CH stretching).

Considering the reaction of the fatty acids (CFA and palmitic acid), these show the disappearance of the broad band between 3,400 and 2,400 cm^{-1}, typically from hydroxyl groups (OH stretching), and the shift of carbonyl group absorption from 1,711 to 1,741 cm^{-1} (C=O stretching), due to conversion of a carbonyl in a carboxylic acid to a carbonyl in an ester group.

For the synthesis from soybean oil, one small shift of carbonyl ester group absorption from 1,746 to 1,741 cm^{-1} is observed, due to the conversion of a triglyceride into an unsaturated ester (CH_2=CH–CH_2–OCO–).

These results confirm the successful synthesis of AFAD from CFA and soybean oil.

GC-FID and GC–MS Characterization

The conjugated fatty acids (CFA) used in this study were a complex mixture used as an industrial raw material. In order to obtain additional information about their composition, fatty acid methyl esters (FAME) were prepared and analyzed by GC-FID. The main components of the FAME derivatives from CFA (Table 1) were fatty acids with two conjugated double bonds (18:2, 48 %, conjugated linoleic acids, CLA) and one double bond (18:1, 27 %). The chromatographic profile of FAME and AFAD are compared in Fig. 4a, b. Although there is a shift in retention times for all AFAD components, in relation to those in FAME, the two chromatographic profiles are essentially the same. For example, the retention time of allyl palmitate (16:0, $t = 18$ min) is delayed in relation to the methyl ester ($t = 15$ min) due to the higher molecular weight.

The functionalization of CFA with an allyl group was further confirmed by GC–MS. The mass spectrum of allyl palmitate (Fig. 4c) was characterized by a molecular ion (M) at $m/z = 296$, the acylium ion at $m/z = 239$ $[\mathrm{M{-}OC_3H_5}]^+$ and by a series of ions at $m/z = 57, 71, 85, 113$, due to the pattern fragmentation of the aliphatic chain of the fatty acid of general formula $[C_nH_{2n\text{-}1}]^+$. Furthermore, the MS spectrum shows the base peak of $m/z = 100$, formed by a McLafferty rearrangement, which is a key fragment of allyl esters from straight-chain acids with a long chain [21].

NMR Spectroscopy

The NMR spectra of the CFA mixture, AFAD from CFA to allyl palmitate are shown in Fig. 5.

The ^{1}H-NMR spectrum of AFAD from CFA, shows the typical resonances of the saturated aliphatic chain ($[(CH_2)_n]$, between δ 0 and 3 ppm, namely at δ 0.85 (*t*, 3H, CH_3, $H_{\text{-}18}$), at δ 1.3 (*m*, aliphatic CH_2, $H_{\text{-}4}$–$H_{\text{-}7}$ and $H_{\text{-}14}$–$H_{\text{-}17}$), at δ1.58 (*m*, 2H, –CH_2–CH_2–C(=O)–, $H_{\text{-}3}$) and at δ 2.26 (*t*, 2H, –CH_2–C(=O)–, $H_{\text{-}2}$).

Even though the region between δ 5 and 6.5 ppm, concerning the aliphatic and allylic double bonds, is difficult to interpret due to the complex CFA mixture used in this study, the comparison with allyl palmitate allows differentiation between the two types of double bonds. It is then possible to identify the three allyl ester protons, namely $H_{\text{-}2'}$ at δ 5.85 ppm (*ddt*, 1H, $J = 17.2$, 10.5 and 5.7 Hz, CH_2=CH–) and 2 $H_{\text{-}3'}$ one at δ 5.28 ppm (*ddt*, 1H, $J = 17.2$, 1.6 and 1.6 Hz, CH_2=CH–) and other at δ 5.14 ppm (*ddt*, 1H, $J = 10.5$, 1.6 and 1.6 Hz, CH_2=CH–) (Fig. 5b). Additionally, the CFA spectrum (Fig. 5a), shows peaks at δ 5.45, δ 5.60, δ 5.95 ppm assigned to protons from conjugated double bonds (CH=CH–CH=CH, C18:2

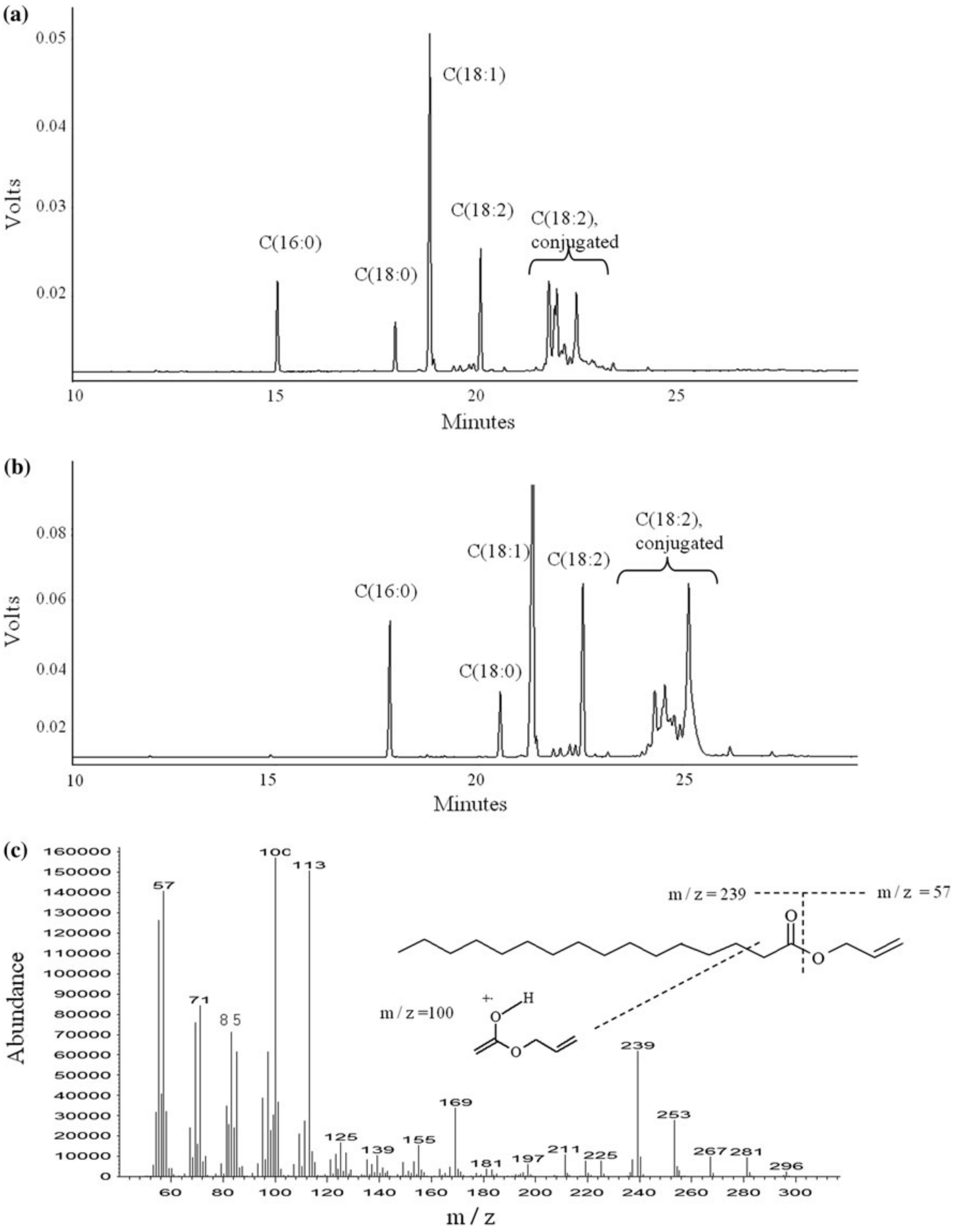

Fig. 4 GC chromatogram of **a** fatty acid methyl esters (FAME) from CFA, **b** AFAD from CFA, **c** mass spectrum of allyl palmitate. 276 × 284 mm (150 × 150 DPI)

Δ^{9Z-11E}), specifically H_{-12}, H_{-10}, H_{-11} [22]. Moreover, the signal at δ 5.28 ppm suiting to H_{-9}, is overlapped by 4H from non-conjugated double bonds (CH=CH–CH_2–CH=CH, C18:2 Δ^{9Z-12E}) from the non conjugated fatty acids of CFA mixture and 2H from oleic acid double bond (C18:1 Δ^{9Z}).

The structure determined by ^{1}H NMR was confirmed by ^{13}C-NMR analysis (Fig. 6). The spectrum of AFAD from

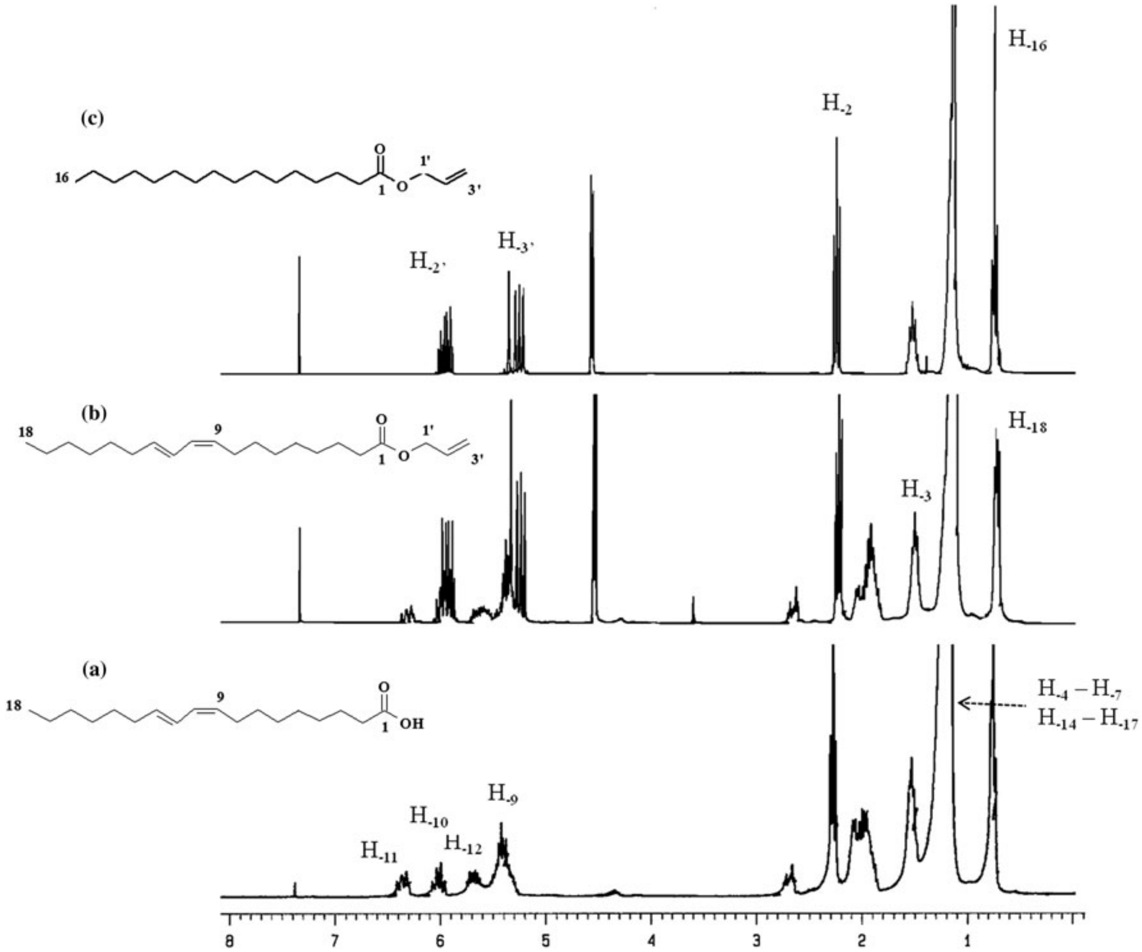

Fig. 5 ^{1}H-NMR spectrum of **a** conjugated fatty acid (CFA), **b** AFAD from CFA, **c** allyl palmitate. 268 × 204 mm (150 × 150 DPI)

CFA is almost identical to that of allyl palmitate, except for the regions between δ 115 and 140 ppm, relative to carbon doubles bonds of unsaturated carbons from the mixture of conjugated fatty acids and from the allylic group. However, it is possible to identify the pair of peaks with higher intensity at δ 117.25 (CH_2=CH–) and 132.11 ppm (CH_2=CH–), as the carbons of the allylic group, namely $C_{-3'}$ and $C_{-2'}$. Additionally, the characteristic signal of $C_{-1'}$ from the allylic group appears at δ 64.39 ppm (CH_2=CH–CH_2O–). The large number of signals with different intensities, in the region assigned to aliphatic chain $[(CH_2)_n]$ between δ 22 and 35 ppm, is according to the mixture of geometric fatty acid isomers with different stereochemistry and unsaturation levels [23, 24].

Film-Forming Behavior

A coalescing agent lowers the film-forming temperatures of a water-borne resin (latex) and thus facilitates the formation of a continuous, homogeneous film at ambient temperature for use in practical applications like coatings. Different amounts of AFAD from CFA, namely 3, 5, and 14 wt%, were added to a commercial acrylic resin, typically used in water-borne paint formulations, and the minimum film-forming temperatures (MFT) evaluated.

Table 2 shows the results obtained. The addition of 5 wt% AFAD decrease the MFT significantly, from 15 to 0 °C. Higher AFAD amounts do not cause any further reduction in MFT. This shows that AFAD effectively act as a coalescing agent.

It is relevant to discuss whether an AFAD can be considered a non-volatile additive in a paint formulation. Compounds are considered as non-volatile if the boiling point is <250 °C at atmospheric pressure [25]. No data was found in literature for unsaturated allyl fatty acid derivatives as AFAD. Considering that, at atmospheric pressure, allyl octanoate (C8:0) has a boiling point of 222 °C [26] and AFAD from the saturated fatty acid (C18:0) has a boiling point of 401 °C [27], it can be expected that AFAD from CFA will also have a boiling point >250 °C. Additionally, a value of 466 °C was estimated for the boiling point of AFAD using the Joback modification of

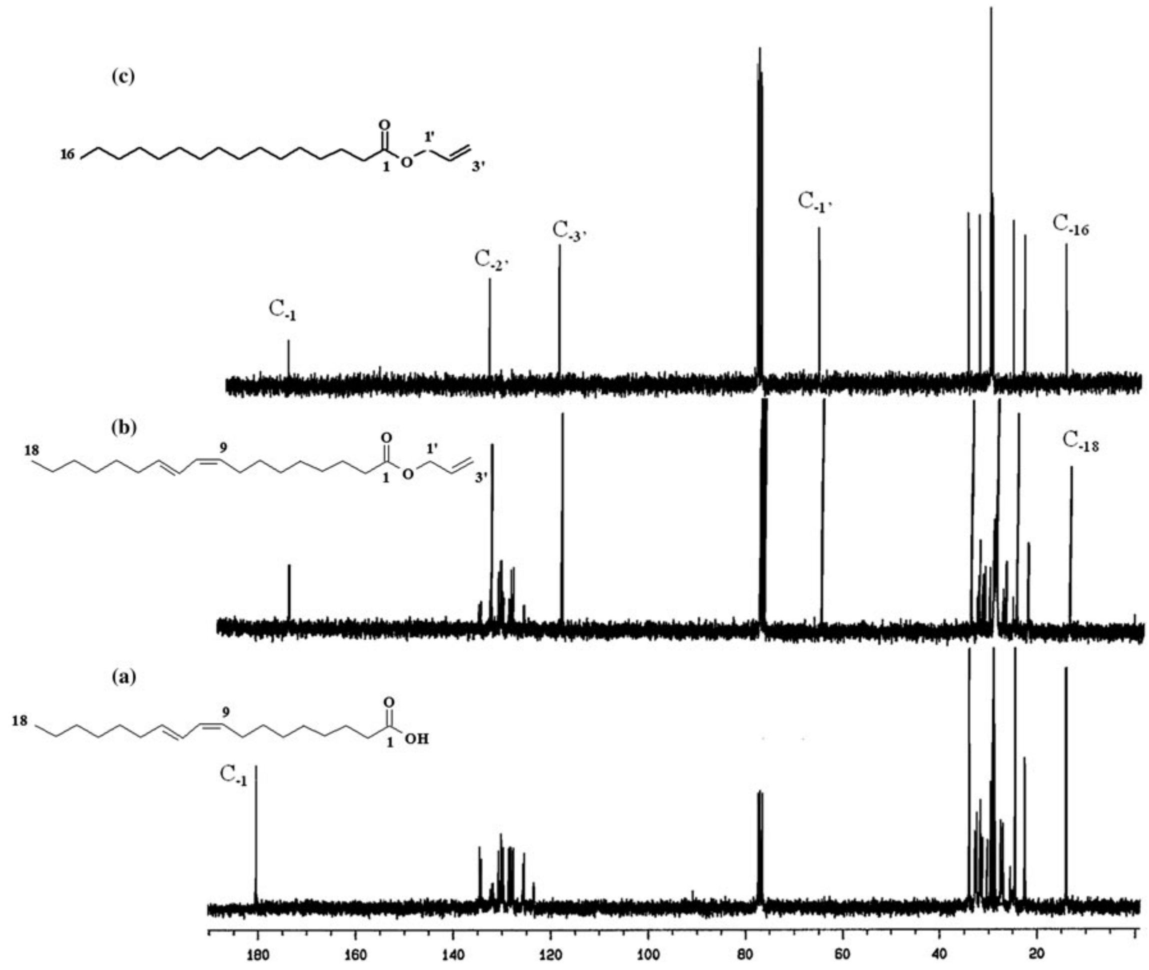

Fig. 6 ^{13}C-NMR spectrum of **a** conjugated fatty acid (CFA), **b** AFAD from CFA, **c** allyl palmitate. 272 × 207 mm (150 × 150 DPI)

Table 2 Minimum film-forming temperature (MFT) of acrylic resins mixtures with an allyl fatty acid derivative (AFAD) from CFA

AFAD from CFA amount (%)	MFT (°C)
0	15
3	9
5	0
14	<0

Lydersen's group contribution method [28]. This confirms that AFAD can be considered a non-volatile component of a commercial formulation.

Oxidative Cure Behavior

It was shown by IR and NMR spectroscopy that the AFAD synthesized from soybean oil and CFA have two double bonds in the aliphatic chain, being conjugated in the second case. These can, in principle, allow for oxidative cure to

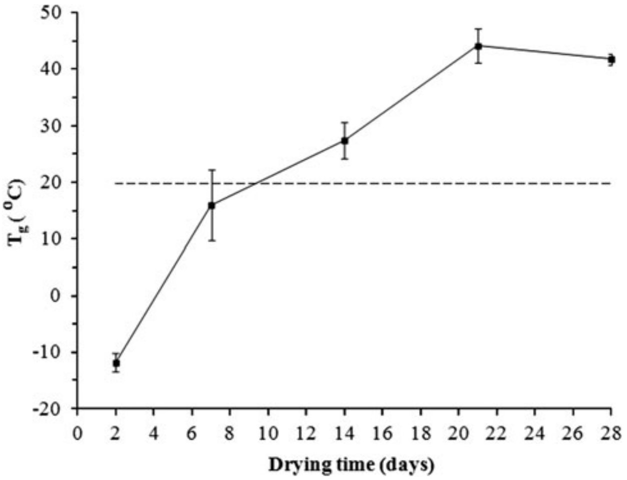

Fig. 7 Glass transition temperature of mixtures of acrylic resin with 5 wt% AFAD from CFA as a function of drying time. The *dashed line* indicates the T_g for the pristine acrylic resin. Error bars represent standard deviations computed from 3 measurements. 158 × 120 mm (96 × 96 DPI)

occur, i.e. ambient temperature crosslinking upon exposure to air by reaction of unsaturated double bonds from adjacent molecules.

Table 3 Drying times of physical mixtures of acrylic resin with 5 % of allyl fatty acid derivative (AFAD)

AFAD type	Driers added	*t* (min)
–	No	45
Palmitic acid	No	45
Soybean oil	No	40
CFA	No	38
–	Yes	41
Palmitic acid	Yes	37
Soybean oil	Yes	36
CFA	Yes	35

Glass transition temperatures (T_g) were measured as a function of drying time, for mixtures of acrylic resin with 5 wt% AFAD from CFA, prepared by vigorous stirring for 30 min. The results are shown in Fig. 7. The T_g of the pristine acrylic resin is also indicated, having a value of 19.6 °C. The T_g of the dry mixture is initially −13 °C, indicating that the AFAD were acting as a plasticizer of the acrylic polymer, facilitating coalescence, as previously shown by the MFT measurements. As time advances, the T_g increases considerably, eventually stabilizing above 40 °C, after 22 days. This indicates progressive hindrance of molecular mobility, due to the occurrence of crosslinking within the dry film, which can only be ascribed to oxidative cure of AFAD from CFA.

Drying time tests were performed on mixtures of acrylic resin with 5 wt% of the different synthesized AFAD. These tests evaluate the time needed for the film surface to become dry to the touch. Mixtures were tested with and

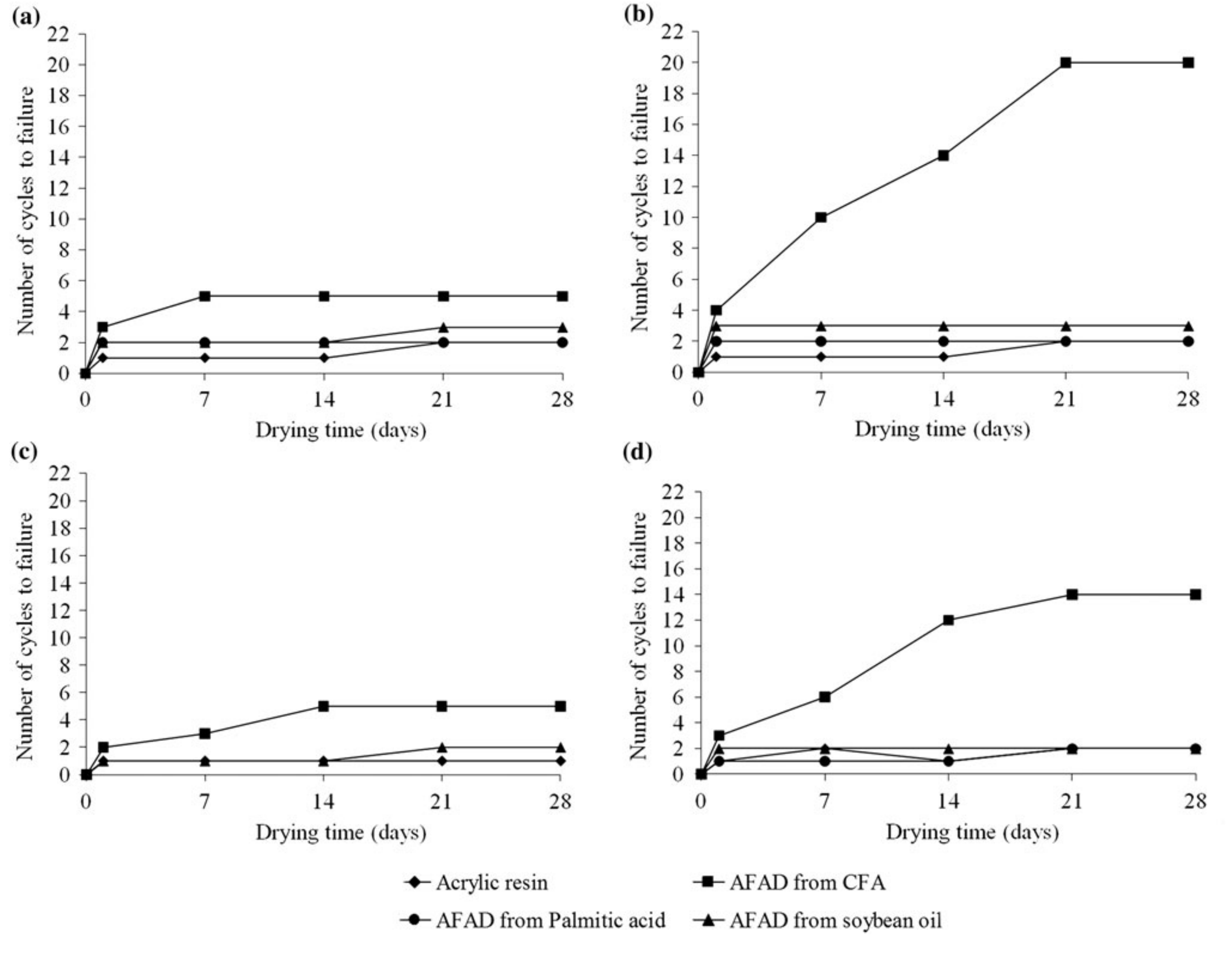

Fig. 8 Rubbing resistance of acrylic resin and AFAD from CFA mixtures using two solvents **a** xylene without driers, **b** xylene with drier agents, **c** acetone without driers, **d** acetone with driers. 292 × 220 mm (150 × 150 DPI)

without addition of drier agents. These are a commercial catalyst combination (a mixture of cobalt, zinc and zirconium) typically used for accelerating the drying rate of alkyd paints [1, 29, 30]. Table 3 shows the results obtained. As expected, the pristine acrylic resin and its mixture with allyl palmitate (16:0) have identical drying times (45 min), not being expected to exhibit oxidative cure. On the other hand, the AFAD from soybean oil (18:1) cause the drying time to be shortened (40 min). The value is even lower for AFAD from CFA (38 min), probably due to the higher reactivity of the conjugated double bonds. This result indicates the occurrence of oxidative cure at the film surface within a short time. As expected, these effects are more evident when driers are present (36 and 35 min, respectively).

To evaluate the “through-dry state” of the film, i.e. whether the film has dried effectively along its depth, a rubbing resistance test was performed, using two solvents of different polarity—xylene and acetone. This was evaluated for 1, 7, 14, 21 and 28 days of air exposure at ambient temperature, with and without driers. In the xylene resistance test (Fig. 8a, b), mixtures with allyl palmitate and soybean oil had the same behavior as the acrylic resin (<3 cycles to failure after 28 days), even when driers were added. The mixture with AFAD from CFA without driers showed a slightly better performance (5 cycles to failure), within 7 to 14 days of drying. But when driers were added (Fig. 8b), the final performance was remarkably better (20 cycles to failure). The combination of AFAD from CFA with the catalyst mixture led to an effective oxidative cure throughout the film.

The rubbing resistance tests with acetone (Fig. 8c, d) showed equivalent results, but the performance of AFAD from CFA with driers is not as good (14 cycles to failure). The acrylic resin has a higher affinity towards a polar solvent like acetone, which weakens the rubbing resistance. The formation of polar groups along the aliphatic chain during the oxidative cure process, namely, ketones, alcohols and carboxylic acids, may also facilitate solvent penetration in the film [30].

Conclusions

Allylic fatty acid derivatives (AFAD) were successfully synthesized by two-step esterification from a mixture of conjugated fatty acids. The reaction progress was followed by FT-IR. The chemical structure of the final products was confirmed by FT-IR and NMR, namely the presence of conjugated double bonds in the aliphatic chain.

When blended with a commercial acrylic latex, AFAD have a noticeable effect on the minimum film-forming temperature, decreasing it from 15 to 0 °C. Additionally, the presence of aliphatic double bonds allows for oxidative cure to occur, as demonstrated by the increase in glass transition temperature and improvement on rub resistance with air exposure time.

AFAD have therefore potential interest as non-volatile additives in waterborne coatings, acting as coalescing agents and autoxidative crosslinking agents. This may contribute to minimizing the use of volatile coalescing agents, with clear environmental and health benefits.

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References

1. Turner GPA (1988) Introduction to paint chemistry and principles of paint technology, 3rd edn. Chapman & Hall, London
2. Lazzari M, Chiantore O (1999) Drying and oxidative degradation of linseed oil. Polym Degrad Stabil 65:303–313
3. Christensen PA, Egerton TA, Lawson EJ (2002) Measurement of carbon dioxide evolution from alkyd paints. J Mater Sci 37:3667–3673
4. van Gorkum R, Bouwman E (2005) The oxidative drying of alkyd paint catalysed by metal complexes. Coord Chem Rev 249:1709–1728
5. Pelletier H, Gandini A (2006) Preparation of acrylated and urethanated triacylglycerols. Eur J Lipid Sci Technol 108:411–420
6. Thames SF, Panjnani KG, Fruchey OS (1999) Latex compositions containing ethylenically unsaturated esters of long-chain alkenols. US Patent 6,001,913
7. Saam JC (2001) Air curing water base copolymers and method of preparation. US Patent 6,177,510
8. Quintero C, Mendon SK, Smith OW, Thames SF (2006) Miniemulsion polymerization of vegetable oil macromonomers. Prog Org Coat 57:195–201
9. Booth G, Delatte DE, Thames SF (2007) Incorporation of drying oils into emulsion polymers for use in low-VOC architectural coatings. Ind Crop Prod 25:257–265
10. Wood A (2003) Archer Daniels Midland starts shipments of zero-voc coalescing agent. Chem Week 165(5):22–22
11. Yang Y, Sheerin R, Shavel LC (2009) Paint compositions with low- or zero-voc coalescence aids and nano-particle pigments US Patent 20090149591 A1
12. Muizebelt WJ, Hubert JC, Nielen MWF, Klaasen RP, Zabel KH (2000) Crosslink mechanisms of high-solids alkyd resins in the presence of reactive diluents. Prog Org Coat 40:121–130
13. van Gorkum R, Bouwman E (2005) Coord Chem Rev 249:1709–1728
14. Chang S-H, Miwa TK (1979) Allyl esters of crambe-derived long-chain fatty acids and their polymers. J Appl Polym Sci 24:441–454
15. Chow RCL, Marvel CS (1968) Copolymerization of allyl esters of some fatty acids. J Polym Sci Part A-1 6:1515–1521

16. Sandler SR, Karo W (eds) (1996) Polymerization of allyl esters. In: Polymer syntheses, vol 3, 2nd edn. Elsevier Science and Technology Books, New York, pp 281–329
17. Palmese GR, La Scala JJ, Sands JM (2009) Fatty acid monomers to reduce emissions and toughen polymers. U.S. Patent 7,534, 909 B2
18. Freedman B, Pryde EH, Mounts TL (1984) Variables affecting the yields of fatty esters from transesterified vegetable oils. J Am Oil Chem Soc 61:1638–1643
19. De Filippis P, Giavarini C, Scarsella M, Sorrentino M (1995) Transesterification process for vegetable oils: a simple control method of methyl ester content. J Am Oil Chem Soc 72:1399–1404
20. Dias J, Alvim-Ferraz MC, Almeida MF (2008) Comparison of the performance of different homogeneous alkali catalysts during transesterification of waste and virgin oils and evaluation of biodiesel quality. Fuel 87:3572–3578
21. Escribà M, Barbut M, Eras J, Canela R, Avila J, Balcells M (2009) Synthesis of allyl esters of fatty acids and their ovicidal effect on *Cydia pomonella* (L.). J Agric Food Chem 57:4849–4853
22. Lie Ken Jie MSF (2001) Analysis of conjugated linoleic acid esters by nuclear magnetic resonance spectroscopy. Eur J Lipid Sci Tech 103:594–632
23. Lie Ken Jie MSF, Mustafa J (1997) High-resolution nuclear magnetic resonance spectroscopy-applications to fatty acids and triacylglycerols. Lipids 32:1019–1034
24. Davis AL, McNeill GP, Caswell DC (1999) Analysis of conjugated linoleic acid isomers by ^{13}C NMR spectroscopy. Chem Phys Lipids 97:155–165
25. Directive 2004/42/CE of the European Parliament and of the Council, 21 April 2004, Official Journal of the European Union, L 143/87 - L 143/96
26. ChemIndex 2011, CAS number: 6289-31-2. www.chemindex.com http://www.chemindex.com/index/?f=show_cas_info&terms=6289-31-2+. Accessed Sept. 2011
27. ChemIndex 2011, CAS number: 4230-97-1. www.chemindex.com. http://www.chemindex.com/index/?f=show_cas_info&terms=4230-97-1. Accessed Sept. 2011
28. Reid RC, Prausnitz JM, Poling BE (1987) The properties of gases & liquids, 4th edn. McGraw-Hill, New York, pp 11–27
29. Mallégol J, Lemaire J, Gardette J (2000) Drier influence on the curing of linseed oil. Prog Org Coat 39:107–113
30. Holmberger K et al (2003) Surfactants and polymers in aqueous solution, 2nd edn. Wiley, Chichester, p 14