1 Incorporation of an acrylic fatty acid derivative as comonomer for oxidative cure in

2 acrylic latex

3

4 Joana V. Barbosa [a], Jorge Moniz [b], Adélio Mendes [a], Fernão D. Magalhães [a], Margarida M.S.M.

5 Bastos [a]1

6

7 [a] LEPAE - Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do

8 Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

9 [b] Resiquímica – Resinas Químicas, S.A., Rua Francisco Lyon de Castro, 28, 2725-397 Mem

10 Martins, Lisboa, Portugal

11
12

1 Corresponding author. Tel.: +351 22 5081648; Fax: +351 22 5081449. E-mail address: mbastos@fe.up.pt.

1

2 Abstract

3 An acrylic fatty acid derivative (AcFAD) was evaluated as comonomer for promotion of oxidative

4 cure in waterborne latexes. AcFAD was polymerized by solvent homopolymerization and

5 copolymerization and by emulsion copolymerization, and the final products characterized. In the

6 two polymerization processes, NMR analyses confirmed that the reaction occurred involving both

7 the terminal acrylic double bond and the conjugated double bonds of the aliphatic chain.

8 Compared with a reference acrylic latex, the results obtained after AcFAD incorporation showed

9 time-dependent increase in gel content and in solvent resistance of dry films. These were ascribed to

10 oxidative cure and consequent self-crosslinking of the acrylic polymer, involving the conjugated

11 double bonds in AcFAD side-chains. Oxidative cure was also confirmed by FT-IR analyses. In

12 addition, reduction in minimum film-forming temperature (MFT) evidenced that AcFAD has an

13 internal plasticization effect during film formation. Incorporation of this comonomer in acrylic paint

14 binder formulations constitutes a promising alternative to the use of volatile coalescing agents.

15

16 Keywords: Acrylic fatty acid derivative; Emulsion polymerization; Oxidative cure; Acrylic latex;
17 Reactive coalescing agent

18

19

20

21

22

23

24

25

26

1. Introduction

Environmental regulations are imposing increasing limitations to emission of volatile organic compounds (VOC) to atmosphere, since this ultimately leads to formation of tropospheric ozone and other harmful substances[1]. These regulations are pushing forward the development of low VOC emission paints. One strategy involves reduction of organic solvents in waterborne paints. This implies developing of polymeric binders for paint formulations that are capable of film formation at room temperature without the need for addition of volatile coalescing agents. This may be achieved by taking advantage of the same drying mechanism used in oil-based alkyd paints. A lipid autoxidation process takes place upon solvent evaporation and exposure to atmospheric oxygen, involving conjugated double bonds present in aliphatic side chains[2]; this inter-chain crosslinking process promotes effective film hardening along a relatively short time[3-5]. Vegetable oils, such as castor, linseed and sunflower oil, and their derivatives have been used in paints, varnishes and textiles for many years. Extensive studies have focused on the introduction of acrylic, vinylic, epoxy and styrenic groups in the vegetable oils, usually involving esterification or transesterification reactions[6-8], and evaluate their applicability in homo and copolymerization and in emulsion and miniemulsion polymerizations[9-12].

Incorporation of fatty acid derivatives as comonomers in emulsion polymers has also been suggested as a strategy for obtaining waterborne paints capable of self-crosslinking[13-17]. The oxidative cure mechanism inherent to the presence of conjugated double bonds allows formation of a hard, non-tacky, film surface without evaporation of a coalescing agent. Additionally, the drying rates can be accelerated by addition of catalytic driers[13, 15, 18].

Another approach described in literature is the use of reactive coalescing agents, which remain in the film after drying instead of evaporating into the atmosphere during, therefore minimizing VOC emissions[19-21].

In this study, an acrylic fatty acid derivative (AcFAD) is shown to be suitable for copolymerization in acrylic polymer formulations, providing oxidative cure mechanism to the dry films. Two different approaches to free radical addition polymerization were studied: in solution and in emulsion. In solution polymerization the monomer and the catalyst are dissolved in a non-reactive solvent, while in emulsion polymerization the reaction occurs in surfactant-stabilized micelles containing monomers and growing polymer chains, dispersed in a continuous water phase[22, 23]. The

resulting products from acrylic fatty acid derivatives (AcFAD) homo and copolymerization were characterized, focusing on its potential use.

2. Experimental

2.1. Materials

A mixture of conjugated fatty acids (CFA) derived from sunflower oil, xylene, benzoyl peroxide (BP), methyl methacrylate (MMA), butyl acrylate (BA), acrylic acid (AA), dodecyl benzenesulfonic acid sodium salt (DBSA), fatty alcohol ether sulfosuccinate disodium salt (FAES), ethoxylated alkyl sulphate, sodium persulfate, dibutyltin oxide were kindly supplied by Resiquímica - Resinas Químicas, S.A. (Mem Martins, Portugal). CFA contains 48 wt.% of compounds with two conjugated double bonds (conjugated linoleic acids, CLA), 27 % with one double bond (oleic acid), 11 % with two non-conjugated double bonds (linoleic acid) [15, 16].

18:2, 48 %,) and one double bond (18:1, 27 %)

Methanol was purchased from Merck; deuterated chloroform (CDCl$_3$, 99.8 % D) from Sigma-Aldrich. All chemicals were used as received. The drying catalyst (a combination of cobalt, barium and zirconium) was kindly dispensed by CIN – Corporação Industrial do Norte (Maia, Portugal).

2.2. Characterization methods

^{1}H NMR spectra were acquired on a Bruker Avance III - 400 spectrometer operating at a frequency of 400 MHz, using deuterated chloroform as solvent. Chemical shifts were reported in part per million (ppm, δ) and referenced to CDCl$_3$. Polymer latexes were freeze-dried prior to NMR spectra collection.

Infrared (IR) spectra were recorded with an ABB - Bomen spectrometer, equipped with an ATR cell. Each spectrum was an average of 32 scans taken with 4 cm^{-1} resolution in the 4000-650 cm^{-1} range. Savitzky-Golay method was used, to obtain second derivatives by means of 17 points smoothing filter and a second order polynom[24, 25].

Solid content of the latexes was determined by evaporating the water in pre-weighed dishes in an oven at 105 ºC for 1 h. The results reported are an average for at least three determinations.

Filtration residue was obtained by filtering the final latex with a mesh of 160 μm. The value presented is the ratio between the residue mass and the total latex mass.

Minimum film-forming temperature (MFT) was determined according to standard ISO 2115:1996. MFT was measured using a Rhopoint MFFT 60 instrument.

Viscosity was measured using a Brookfield LV instrument, and all the measurements were made with a Spindle number 2, at 100 rpm rotational speed and at room temperature. pH value was determined at 23 ºC, by electrometric measurement, using a glass electrode.

Zeta potential was determined using a Zetasizer Nano (Malvern). The results reported are an average for at least three determinations.

For the gel content and solvent resistance tests, the dry films of the prepared latexes were prepared by doctor blading on a glass plate. The wet thickness of the films was 200 μm.

Gel content was determined by mixing about 0.0500 g of dried films with 5 mL of toluene, during 1 h at 80 ºC. The solutions were filtered using 0.45 μm nylon filters, which were dried for 5 weeks and weighed until constant weight, in order to determine the amount of insoluble crosslinked material. The values reported are an average of at least three determinations.

Solvent resistance test consists on evaluation of the number of cycles (double rubs) until film failure. Rubbing was performed manually with a piece of white cotton embedded with solvent over a 3 cm of film. The solvents used were xylene and propanone. The values reported are an average result for at least two test runs.

2.3. Solution polymerization of AcFAD

AcFAD was obtained from conjugated fatty acids (CFA) esterification (first step) with ethylene glycol followed by esterification with acryloyl chloride (second step). The process is described in detail in a previous work[15]. The overall reaction is presented in Fig. 1.

For homopolymerization, AcFAD (0.002 mol) was placed with 2 ml of toluene and 2 % (molar % relative to AcFAD) of BP in a 25 ml round bottom flask, equipped with magnetic stirrer, thermometer, nitrogen bubbling and a water condenser. The reaction was carried out with vigorous stirring at 85 ºC for 7 h. After reaction, the polymer was precipitated in methanol and dichloromethane was added to the solid filtered to remove some unreacted monomer. Finally, the solvent was removed under vacuum using a rotary evaporator.

AcFAD (10 % molar) was also copolymerized with MMA (90 % molar). The monomer mixture was placed with 2 ml of toluene and 2 % (molar) of BP into a 25 ml round bottom flask, equipped

with magnetic stirrer, thermometer, nitrogen bubbling and a water condenser. The reaction was carried out with vigorous stirring at 85 °C for 7 h. After reaction, the polymer was precipitated in methanol and dichloromethane was added to the solid filtered to remove some unreacted monomer. Finally, the solvent was removed under vacuum using a rotary evaporator.

2.4. Emulsion copolymerization of AcFAD

The comonomer composition used is based on a commercial acrylic latex formulation where 10 wt.% of the main acrylic monomer mixture was replaced by AcFAD. Surfactant ethoxylated alkyl sulphate was initially used, while dodecyl benzenesulfonic acid sodium salt (DBSA) and fatty alcohol ether sulfosuccinate disodium salt (FAES) were used in a subsequent stage of development.

The latex was synthesised by aqueous free radical emulsion polymerization at 80 °C, carried out in a 250 ml jacketed flask reactor equipped with water condenser, mechanical stirrer, thermometer and nitrogen bubbling system. The reaction temperature was controlled by circulating hot water from a temperature controlled water bath in the reactor jacket. The resins compositions are shown in Table 1. A pre-emulsion was prepared by mixing half of water and half of the surfactant with the monomers (MMA, BA, AA and AcFAD) under vigorous stirring. The remaining surfactant and water were initially charged into the reactor at 80 °C. Simultaneously, the pre-emulsion previously prepared and the sodium persulfate (0.3 wt. %) were fed dropwise into the reactor over a period of 2 h. The pre-emulsion was added in two portions. While the first was added, the remaining portion was kept under stirring to prevent phase separation.

AcFAD: **IR** (cm^{-1}): 3006 (CH, unsaturated stretching), 2924 and 2854 (saturated [$(CH_2)_n$] stretching), 1732 (C=O stretching), 1637 (C=C stretching), 1458 and 1408 (CH_2, CH_3 bending), 1173 (C-O, stretching), 984 and 808 ((CH=CH_2, out-of-plane deformation), 723 (CH_2, rocking). **^{1}H NMR** (CDCl$_3$): δ in ppm (*J* in Hz) = 0.79 (*t*, *J*= 7.2, CH_3, H-18), 1.19 (*m*, 16H, aliphatic CH_2, H-4-H-7 and H-14-H-17), 1.52 (*m*, 2H, -C$\underline{H}_2$-CH_2-C(=O)-, H-3), 1.90-2.06 (*m*, 4H, CH_2 allylic), 2.24 (*t*, *J*= 7.2, -CH_2-C(=O)-, H-2), 2.68 (*t*, 2H, *J*= 6.2, CH_2 doubly allylic), 4.27 (*t*, 2H, COO-C$\underline{H}$2-, *J*= 7.2, H-20) and 4.22 ppm (*t*, 2H, COO-C$\underline{H}$2-, *J*=7.2 Hz, H-19), 5.18 ppm (*dt*, *J*=11.0 and 7.0, H-9), 5.3-5.1 ppm (4H from C18:2 C$\underline{H}$=C$\underline{H}$-CH_2-C$\underline{H}$=C$\underline{H}$ and 2H from C18:1 double bond of the CFA mixture), 5.51 (*dt*, *J*=15.0 and 7.0, H-12), 5.76 (*dd*, 1H, *J*=10.4 and 1.2, C$\underline{H}_2$=CH-, H-23a), 5.80 (*t*, *J*=11.0, H-11), 6.04 (*dd*, 1H, *J*= 17.4 and 10.4, CH_2=C$\underline{H}$-, H-22), 6.24 (*dd*, *J*=15.0 and 11.0, H-10), and 6.33 (*dd*, 1H, *J*=17.4 and 1.2, C$\underline{H}_2$=CH-, H-23b)[15].

Reference Acrylic latex: **IR** (cm^{-1}): 2957 and 2874 (CH_3 stretching, asymmetric and symmetric respectively), 1729 (C=O stretching), 1449 and 1386 (CH_2, CH_3 bending), 1160 and 1147 (C-O,

stretching). **¹H NMR** (CDCl₃): δ in ppm = 0.89 (6H, CH₃ from BA and α-CH₃ syndiotactic from MMA), 1.04 (3H, α-CH₃ isotactic from MMA), 1.39 (2H, -CO-O-CH₂-CH₂-C$\underline{H}$₂-CH₃ from BA), 1.61 (2H, -CO-O-CH₂-C$\underline{H}$₂-CH₂-CH₃ from BA), 1.75-2.51 (2H, CH₂ of the α-methanediyl protons), 3.61 (3H, -O-CH₃ from MMA *racemic* configuration), 3.66 (3H, -O-CH₃ from MMA *meso* configuration), 4.02 (2H, -CO-O-C$\underline{H}$₂-CH₂-CH₂-CH₃ from BA).

Latex B: **IR** (cm⁻¹): 3006 (CH, unsaturated stretching), 2924 and 2854 (saturated [(CH₂)ₙ] stretching), 1732 (C=O stretching), 1637 (C=C stretching), 1458 and 1408 (CH₂, CH₃ bending), 1173 (C-O, stretching), 984 and 808 (CH=CH₂, out-of-plane deformation), 723 (CH₂, rocking). **¹H NMR** (CDCl₃): δ in ppm = 0.88 (CH₃, H₋₁₈ from AcFAD), 0.96 (CH₃ from BA and α-CH₃ syndiotactic from MMA), 1.1-1.4 (α-CH₃ isotactic from MMA, 2 CH₂ from BA, aliphatic CH₂, H₋₄-H₋₇ and H₋₁₄-H₋₁₇, from AcFAD), 1.62 (CH₂, H₋₃, from AcFAD and CH₂ from BA), 2.04 (CH₂ allylic from AcFAD), 2.36 (CH₂, H₋₂ from AcFAD), 2.65 (CH of the α-methanetriyl protons), 2.88 (CH₂ doubly allylic from AcFAD), 3.61 (CH₃ from MMA *racemic* configuration), 3.67 (CH₃ from MMA *meso* configuration), 4.02 (CH₂ from BA), 5.36 (4H from C18:2 C$\underline{H}$=C$\underline{H}$-CH₂-C$\underline{H}$=C$\underline{H}$ and 2H from C18:1 double bond of the CFAs mixture).

3. Results and discussion

3.1. Solvent polymerization

To assess the ability of AcFAD to copolymerize, preliminary studies were focused on solution polymerization. Homopolymerization of AcFAD and copolymerization with MMA were investigated by NMR analyses. Since radical propagation can involve both the aliphatic double bonds and the acrylic group, the spectra of AcFAD and of the homopolymerization or copolymerization products were compared in terms of the ratio of the integrals assigned to the aliphatic conjugated double bonds at δ 6.24, 5.80, 5.51 and 5.18 ppm (H₋₉ to H₋₁₂)[15] and the acrylic double bonds at δ 5.76, 6.04 and 6.33 ppm (H₋₂₃ₐ, H₋₂₂ and H₋₂₃ᵦ respectively).

In homopolymerization, reductions of 43 % in the area of the signals corresponding to acrylic double bonds and of 88 % in the area of the signals of aliphatic conjugated double bonds were observed. The unsaturated polymer obtained had 12 % of conjugated double bonds. Previous works on homopolymerization of long chain vinyl and allyl esters derived from fatty acids have shown that polymerization occurs between the aliphatic double bonds of one molecule and the vinyl or allyl group of another[26-28]. In addition, according to Harrison and Wheeler[26], polymerization through conjugated unsaturation is slightly higher than through unconjugated unsaturation.

In copolymerization of AcFAD with MMA, the results indicated that 99 % of the acrylic double bonds were consumed, indicating that both monomers have been almost completely consumed in the radical copolymerization reaction. Concerning AcFAD's conjugated aliphatic double bonds, one of them was 99 % consumed, while the other was preserved. This higher conversion of AcFAD in presence of MMA is explained in terms of minimization of steric effects involved in homopolymerization of large AcFAD molecules[29].

3.2. Emulsion polymerization

AcFAD was incorporated as a comonomer in a reference acrylic latex (described in section 2.4), replacing 10 wt.% of the monomer mixture (latex A). Except for the monomer composition, the two formulations were identical, namely in terms of the surfactant system used. The properties of both latexes are very similar, as shown in Table 1, except for the MFT, which decreased by about 9 ºC with addition of AcFAD, indicating a plasticization effect.

However, complete incorporation of AcFAD in the acrylic latex was not achieved in this formulation, as demonstrated by the presence of a yellow supernatant liquid in the final product. The surfactant used in the reference acrylic latex formulation (ethoxylated alkyl sulphate) was inefficient to emulsify highly hydrophobic AcFAD in the liquid medium. As a consequence, too large monomer drops were formed, and oil/water interfacial area was not high enough for establishing an adequate diffusional flow into micelles, and AcFAD addition to the growing polymer chain. AcFAD is still acting as a plasticizer in the dry film, as shown by the decrease in MFT, but is not effectively incorporated in the acrylic latex.

Following existing information on emulsion polymerization involving a linolenic acid derivative[30], the surfactant was replaced by a combination of dodecyl benzenesulfonic acid sodium salt – DBSA - and fatty alcohol ether sulfosuccinate disodium salt - FAES. Combination of surfactants with different hydrophilic-lipophilic balance (HLB) values is often used in emulsion polymerization [22, 31-34]. The polymerization product remained stable along several weeks and no evidence of yellow supernatant was observed. As seen in Table 1, the MFT for this formulation (latex B) is significantly lower than for the previous cases (18 ºC lower than the reference), indicating a more effective intrinsic plasticization effect, associated with the presence of long aliphatic side chains from AcFAD in the polymer. This originates higher segment mobility through increased intermolecular distance[31], eliminating the need for coalescing agent additives.

Latex B and the reference acrylic latex were stable, showing zeta potential values lower than -30 mV, specifically, -95 mV and -83 mV, respectively. Latexes with zeta potential values between -30

mV and + 30 mV are most often unstable and prone to coagulation, unless a steric stabilization mechanism is present[35].

AcFAD copolymerization with MMA and BA in latex B was confirmed by NMR (Fig. 2) and the chemical shift values were attributed according to the poly(methyl acrylate) (PMA) and poly(methyl methacrylate) (PMMA) values given in the literature[36-39]. Comparing the spectra of the latex copolymerized with AcFAD (Fig. 2b) and the reference acrylic latex (Fig. 2c) the following differences were observed: presence of the signals at δ 2.36 ($-CH_2-C(=O)-$, H_{-2}) and δ 0.88 ppm (CH_3, H_{-18}), from the non-acrylated region of the AcFAD, and the signal at δ 2.65 ppm, attributed to the CH of the α-methanetriyl protons formed during the acrylated copolymerization reaction. On the other hand, a signal around δ 1.20 ppm, assigned to aliphatic CH_2 ($H_{-4}-H_{-7}$ and $H_{-14}-H_{-17}$) of AcFAD (which is not present in the reference emulsion) was observed and the acrylic double bond signals (at δ 5.76, 6.04 and 6.33 ppm, H_{-23a}, H_{-22} and H_{-23b} respectively) disappeared, indicating complete polymerization of AcFAD[38].Due to the relatively low amount of AcFAD present (only 10 wt. % of AcFAD was added and the fraction of CFA in the commercial CFA mixture used is 50 %[15]), the intensity of the signals assigned to the conjugated ($C\underline{H}=C\underline{H}-C\underline{H}=C\underline{H}$, C18:2) and non-conjugated ($C\underline{H}=C\underline{H}-CH_2-C\underline{H}=C\underline{H}$, C18:2) double bonds were difficult to detect. However, by comparing the ratio of the integrals assigned to the doubly allylic CH_2 (at 2.88 ppm) in AcFAD and the latex copolymerized with AcFAD, was verified that 95 % of one double bond from the non-conjugated double bonds was consumed. Nevertheless, there are at least 22 % of conjugated double bonds and portions of polymerized chains with one double bond available for oxidative cure.

To evaluate the oxidative cure behaviour (since NMR confirmed the presence of double bonds) of latex B, the gel content of films dried for up to five weeks was determined and compared with the reference acrylic latex (Fig. 3). The films obtained were homogeneous, non-tacky and clear. Although some crosslinking may have occurred during the polymerization reaction, no gel content was observed in latex B at the beginning of the drying period. The results indicate a final gel content of 6 wt.% for the reference, and of 60 wt.% in latex B. This demonstrates occurrence of auto-crosslinking in latex B. This phenomenon is represented in Fig. 4, showing the formation of peroxide bonds by reaction between the conjugated double bonds in AcFAD's aliphatic chains and atmospheric oxygen. This is just an example of the type of bonds that can be formed in oxidative cure[15, 41].

FT-IR analyses of films dried in air for five weeks also confirmed occurrence of oxidative cure. Since the acrylic latex formulated with AcFAD displays a complex spectrum, causing overlapping and suppression of bands, the analysis was based on the second derivative spectra (Fig. 5). Some differences were observed between the spectra obtained after one day and after five weeks of

drying: i) slight reduction in the intensity of the bands at 2924 and 2854 cm^{-1} (symmetric and asymmetric $(CH_2)_n$), due to hydrogen abstraction on a methylene group on the allylic position[3, 15], and ii) slight decrease in the intensity of the band at 3006 cm^{-1}, assigned to the double bonds of the aliphatic chain (CH, unsaturated stretching), due to the high reactivity towards radical addition of the conjugated double bonds[42, 43]. The decrease in the intensity of the band at 723 cm^{-1}, assigned to the out-of-plane deformation of CH=CH, was not so evident, since it is overlapped by the [$(CH_2)_n$] rocking vibration of the aliphatic chain[15]. It was also noticed that, in films containing catalytic driers, reaction with atmospheric oxygen was very fast, making it impossible to detect the bands related to the formation of hydroperoxide bonds at 3400 cm^{-1} [44].

The solvent resistance of latex B was evaluated and compared to the reference acrylic latex, for films dried up to 5 weeks (Fig. 6). Solvents of different polarities, xylene and propanone, were used on the tests. Latex B showed a much higher resistance towards rubbing with both solvents than the reference acrylic latex. In addition, solvent resistance increased significantly during the drying time, which again confirms that oxidative cure occurs progressively, due to the presence of the AcFAD as comonomer in the latex formulation.

4. Conclusions

An acrylic fatty acid derivative (AcFAD) was tested in solvent homopolymerization and copolymerization and the final products were characterized by NMR. The results showed that the reactions involved the acrylic double bond and the conjugated double bonds. In homopolymerization around 43 % of the acrylic double bonds and about 88 % of the conjugated double bonds were consumed. In copolymerization 99 % of the both type of double bonds were consumed.

Experiments using AcFAD as comonomer in acrylic emulsion polymerization were performed. NMR analyses confirmed that copolymerization occurred, involving the acrylic double bonds, and maintaining a significant number of unsaturations. Resistance to solvents (xylene and propanone) and gel content were significantly higher for the latex containing AcFAD than for the reference acrylic latex. These results, together with FT-IR analyses with application of mathematical spectra treatment (second derivative), showed that oxidative cure took place upon film drying. Additionally, the MFT was considerably lower for the latex with AcFAD, indicating an intrinsic plasticization effect.

AcFAD has potential interest as comonomer in acrylic binders for waterborne paints, since it acts as intrinsic coalescing agent and as a promoter of autoxidative cure. This may provide an alternative to

the use of co-solvents, such as coalescing agents, in this type of paints, therefore reducing VOC emissions in the final product.

References

[1] Information Research Limited, A profile of the West European Paint and Coatings Industry, 2002.

[2] Turner, GPA, Introduction to paint chemistry and principles of paint technology. 3rd ed., Chapman and Hall, London (1988)

[3] Lazzari, M, Chiantore, O, "Drying and oxidative degradation of linseed oil." Polym. Degrad. Stabil., 65 303-313 (1999)

[4] Christensen, PA, Egerton, TA, Lawson, EJ, "Measurement of carbon dioxide evolution from alkyd paints." J. Mater. Sci., 37 3667-3673 (2002)

[5] Quintero, C, Mendon, SK, Smith, OW, Thames, SF, "Miniemulsion polymerization of vegetable oil macromonomers." Prog. Org. Coat., 57 195–201 (2006)

[6] Pelletier H, Gandini A, "Preparation of acrylated andurethanated triacylglycerols". Eur. J. Lipid Sci. Technol., 108 411–420 (2006)

[7] Rengasamy, S, Mannari, V, "Development of soy-based UV-curable acrylate oligomers and study of their film properties". Prog. Org. Coat., 76 78-85 (2013)

[8] Espinosa, LM, Ronda, JC, Galià, M, Cádiz, V, "A New Route to Acrylate Oils: Crosslinking and Properties of Acrylate Triglycerides from High Oleic Sunflower Oil". J. Polymer Sci.: Part A: Polymer Chemistry, 47, 1159-1167 (2009)

[9] Bunkera, S, Stallerb, C, Willenbacherb, N, Wool, R, "Miniemulsion polymerization of acrylated methyl oleate for pressure sensitive adhesives". International Journal of Adhesion & Adhesives, 23 29-38 (2003)

[10] Cho, H, Park, S, Jegal, J, Song, B, Kim, H, "Preparation and Characterization of Acrylic Polymers Based on a Novel Acrylic Monomer Produced from Vegetable Oils". J. Appl. Polym. Sci., 116 736-742 (2010)

[11] Xia, Y, Larock, RC, "Vegetable oil-based polymeric materials: synthesis, properties, and applications". Green Chem., 12 1893-1909 (2010)

[12] Guo, J, Schork, FJ, "Hybrid Miniemulsion Polymerization of Acrylate/Oil and Acrylate/Fatty Acid Systems". Macromol. React. Eng., 2 265-276 (2008)

[13] Thames, SF, Panjnani, KJ, Fruchey, OS, "Latex compositions containing ethylenically unsaturated esters of long-chain alkenols." U.S. Patent 6,001,913, 1999

[14] Thames, SF, Rawlins, JW, Mendon, SK, Johnson, EN, Yu, Z, "Functionalized vegetable oil derivatives, latex compositions and textile finishes." U.S. Patent 0236467, 2006

[15] Barbosa, JV, Veludo, E, Moniz, J, Magalhães, FD, Bastos, MMSM, "Synthesis and characterization of acrylic fatty acid derivative and use as reactive coalescing agent." Eur. J. Lipid Sci. Technol., 114 1175-1182 (2012)

[16] Barbosa, JV, Oliveira, F, Moniz, J, Magalhães, FD, Bastos, MMSM, "Synthesis and characterization of allyl fatty acid derivatives as reactive coalescing agents for latexes." J. Am. Oil Chem. Soc., 89 2215-2226 (2012)

[17] Kaya, E, Mendon, SK, Delatte, D, Rawlins, JW, Thames, SF "Emulsion Copolymerization of Vegetable Oil Macromonomers Possessing both Acrylic and Allylic Functionalities". Macromol. Symp., 324 95-106 (2013)

[18] Gorkum, R, Bouwman, E, "The oxidative drying of alkyd paint catalysed by metal complexes." Coord. Chem. Rev., 249 1709–1728 (2005)

[19] Zhou, L, Pakenham, D, Ruiz, J, Aymes, C., Veres, K, Koltisko, B, "Low VOC coalescing agents." U.S. Patent 8,106,239, 2012

[20] Wood, A, Chemical Week. 165 22-22 (2003)

[21] Yang, Y, Sheerin, R, Shavel, LC, "Paint Compositions with Low-or Zero-VOC Coalescence Aids and Nano-Particle Pigments." U.S. Patent 0149591 A1, 2009

[22] Sperling, LH, Introduction to physical polymer science. 4th ed., Bethlehem, John Wiley & Sons, Pennsylvania (2006)

[23] Matyjaszewski, K, Davis, TP, Handbook of Radical Polymerization, John Wiley & Sons, Hoboken (2002)

[24] Savitzky, A, Golay, MJE, "Smoothing and Differentiation of Data by Simplified Least Squares Procedures." Analytical Chem., 36 1627–1639 (1964)

[25] Meissl, K, Smidt, E, Schwanninger, M, "Prediction of humic acid content and respiration activity of biogenic waste by means of Fourier transform infrared (FTIR) spectra and partial least squares regression (PLS-R) models." Talanta, 72 791–799 (2007)

[26]. Harrison, SA, Wheeler, DH, "The polymerization of vinyl and allyl esters of fatty acids." J. Am. Chem. Soc. 73 839-842 (1951)

[27] Sandler, SR, Karo, W, Polymer Syntheses, 2nd ed., Vol 3, Elsevier Science & Technology Books, London (1996)

[28] Chang, SP, Miwa, TK, "Allyl esters of crambe-derived long-chain fatty acids and their polymers." J. Appl. Polym. Sci., 24 441-454 (1979)

[29] Vilela, C, Rua, R, Silvestre, JD, Gandini, A, "Polymers and copolymers from fatty acid-based monomers." Ind. Crop Prod., 32 97-104 (2010)

[30] Saam, JC, "Glycol co-esters of drying-oil fatty acid made via biphasic catalysis and resulting products." US Patent 5,750,751, 1998

[31] Acosta, EJ, Yuan, JS,. Bhakta, AS, "The Characteristic Curvature of Ionic Surfactants." J. Surfact Deterg., 11 145–158 (2008)

[32] Kosswig, K, "Surfactants." In: Ullmann's - encyclopedia of industrial chemistry (2005)

[33] Moayed, SH, Fateme, S, Pourmahdian, S, "Synthesis of a latex with bimodal particle size distribution for coating applications using acrylic monomers." Prog. Org. Coat., 60 312-319 (2007)

[34] Stamm, M, "Polymers surface and interfaces – Characterization, Modification and Applications." 1st ed., Springer, Berlin (2008)

[35] Lampman, S, "Characterization and Failure Analysis of Plastics." ASM International, pg 35, 2003.

[36] Tan, B, Grijpmaa, DW, Nabuursb, T, Feijen, J, "Crosslinkable surfactants based on linoleic acid-functionalized block copolymers of ethylene oxide and 3-caprolactone for the preparation of stable PMMA lattices." Polymer, 46 1347–1357 (2005)

[37] Brar, AS, Singh, G, Shankar, R, "Structural investigations of poly(methyl methacrylate) by two-dimensional NMR.", J. Mol. Struct., 703 69-81 (2004)

[38] Brar, AS, Goyal, AK, Hooda, S, "Two-dimensional NMR studies of acrylate copolymers." Pure Appl. Chem., 81 389–415 (2009)

1   [39] Mark JE, "Physical Properties of Polymers.", 2nd ed., Springer, New York (2007)

2   [40] Booth, G, Delatte, DE, Thames, SF, "Incorporation of drying oils into emulsion polymers for

3   use in low-VOC architectural coatings." Ind. Crop. Prod., 25 257–265 (2007)

4   [41] Cheong, MY, Ooi, TL, Ahmad, S, Yunus, WMZW, Kuang, D, "Synthesis and characterization

5   of palm based resin for UV coating." J. Appl. Polym. Sci., 111 2353-2361 (2008)

6   [42] Mallégol, J, Gardette, J, Lemaire, J, "Long-Term Behavior of Oil-Based Varnishes and Paints

7   I. Spectroscopic Analysis of Curing Drying Oils." J. Am. Oil Chem. Soc., 76 967-976 (1999)

8   [43] Mallégol, J, Gardette, J, Lemaire, J, "Drier influence on the curing of linseed oil." Prog. Org.

9   Coat., 39 107–113 (2000)

10   [44] Mallégol, J, Gardette, J, Lemaire, J, "Long-Term Behavior of Oil-Based Varnishes and Paints.

11   Photo- and Thermooxidation of Cured Linseed Oil." J. Am. Oil Chem. Soc.. 77 257–263 (2000)

12

13

First step

CFA   EG   FAGE

Second step

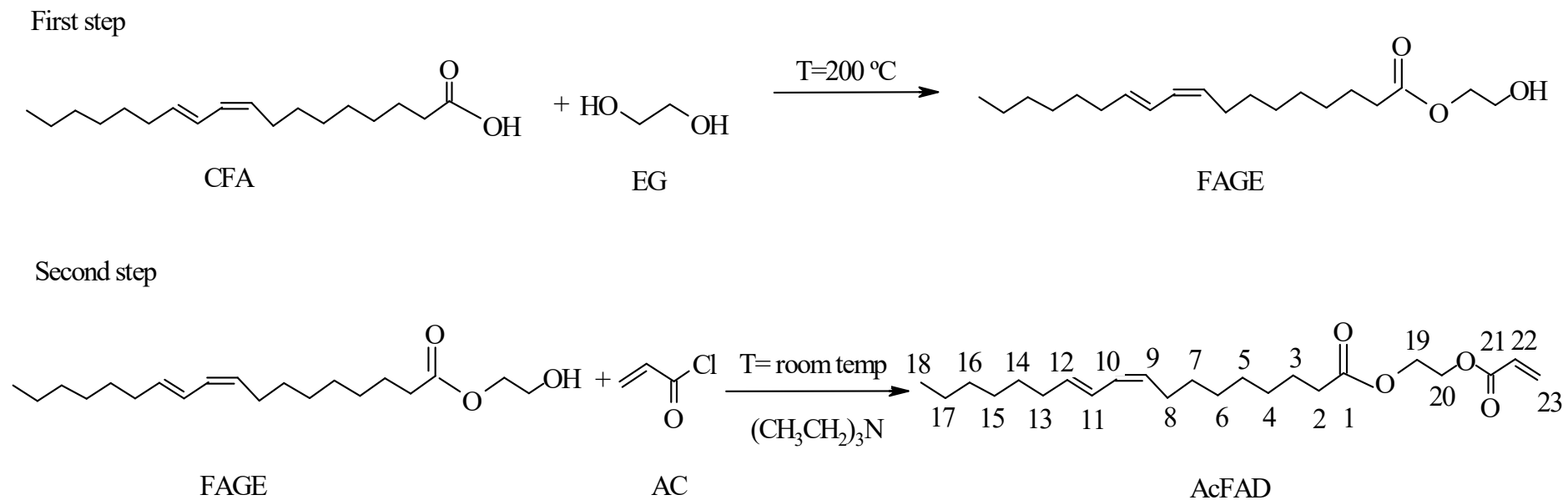

FAGE   AC   AcFAD

Fig. 1 – Scheme of the reactions involved on AcFAD synthesis process (AcFAD structure represents the main component of the conjugated fatty acid).
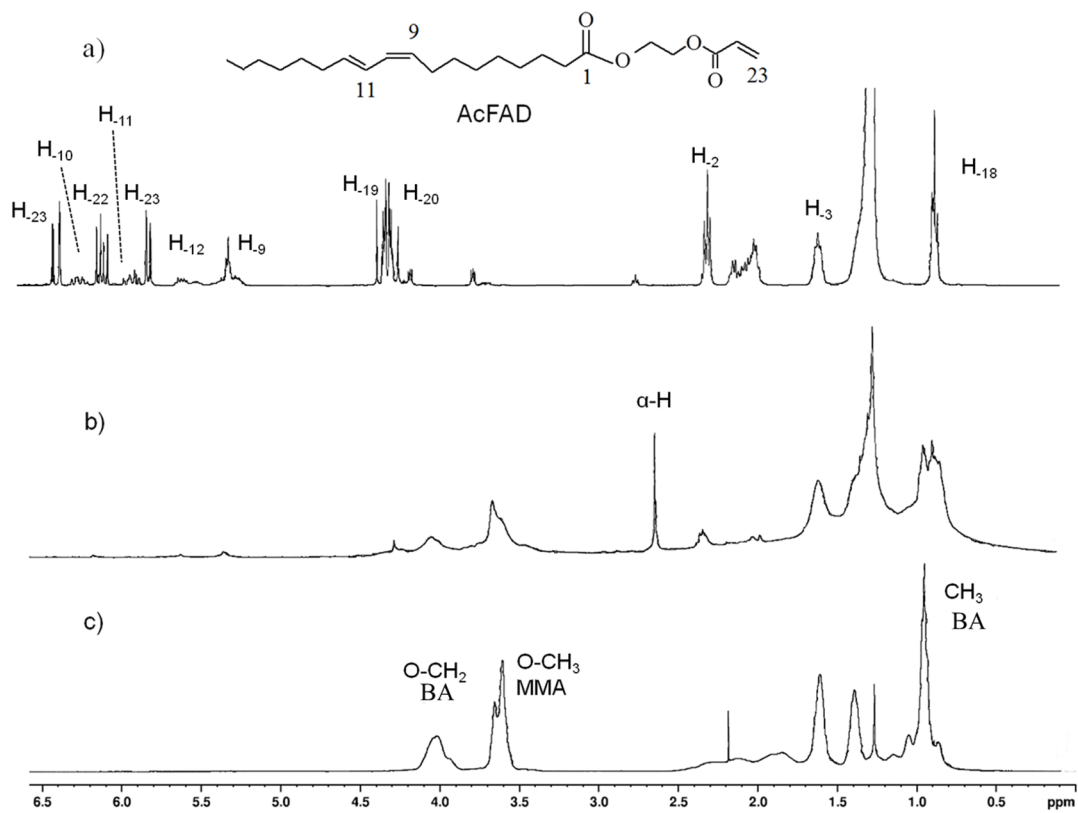
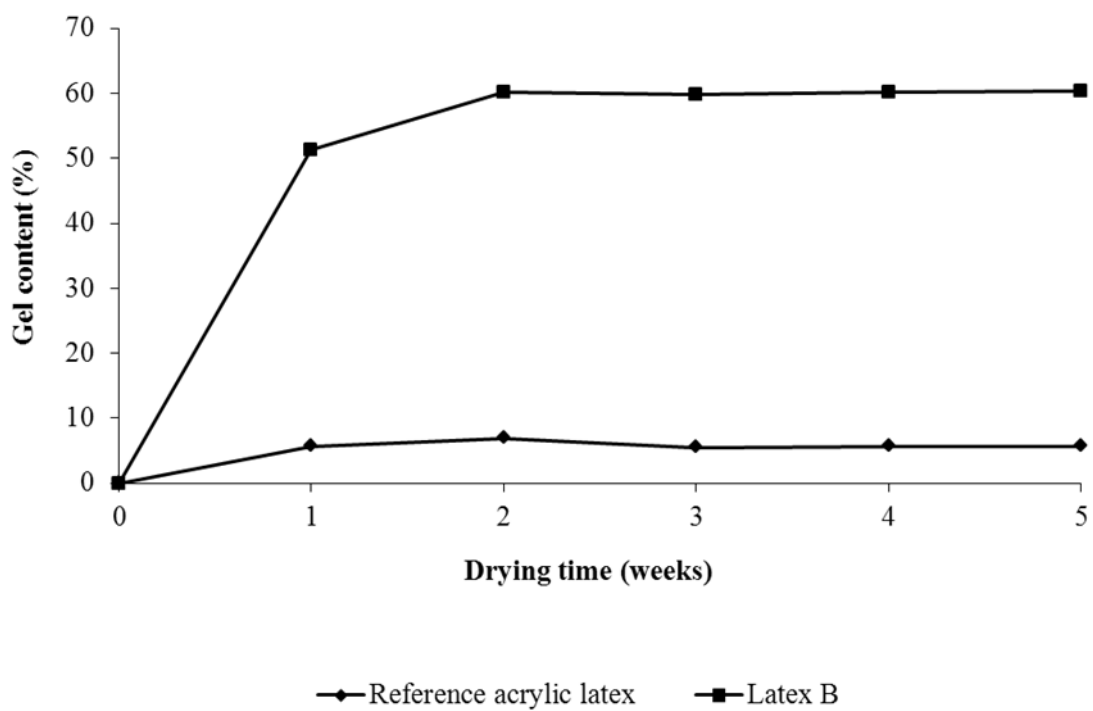Fig. 2 - 1H-NMR spectrum of a) AcFAD, b) latex B and c) reference acrylic latex.

Fig. 3 – Gel content of latex B (copolymerized with AcFAD) and reference acrylic latex along drying time (AcFAD structure represents one of the possible CFAs derivatives).
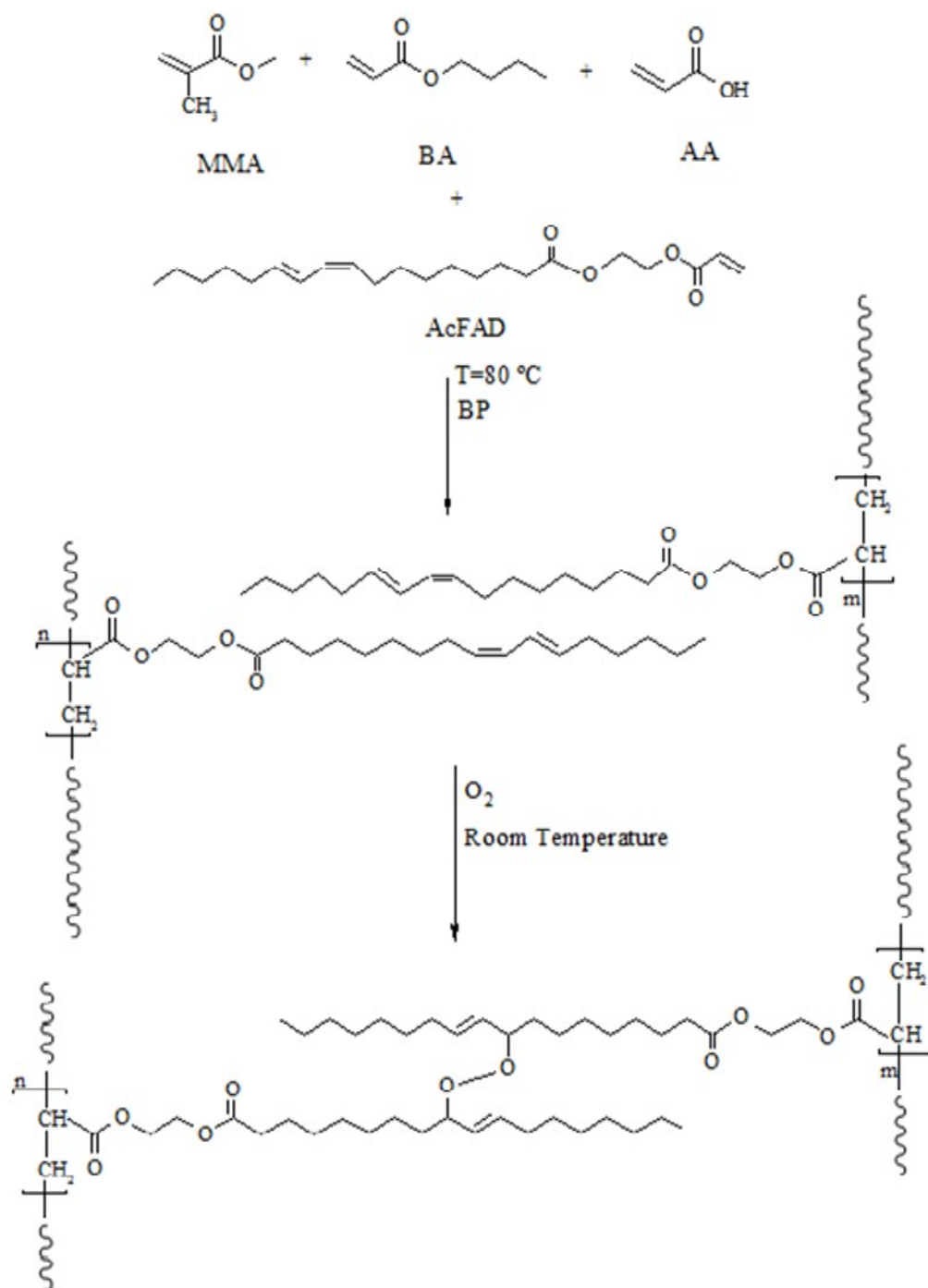
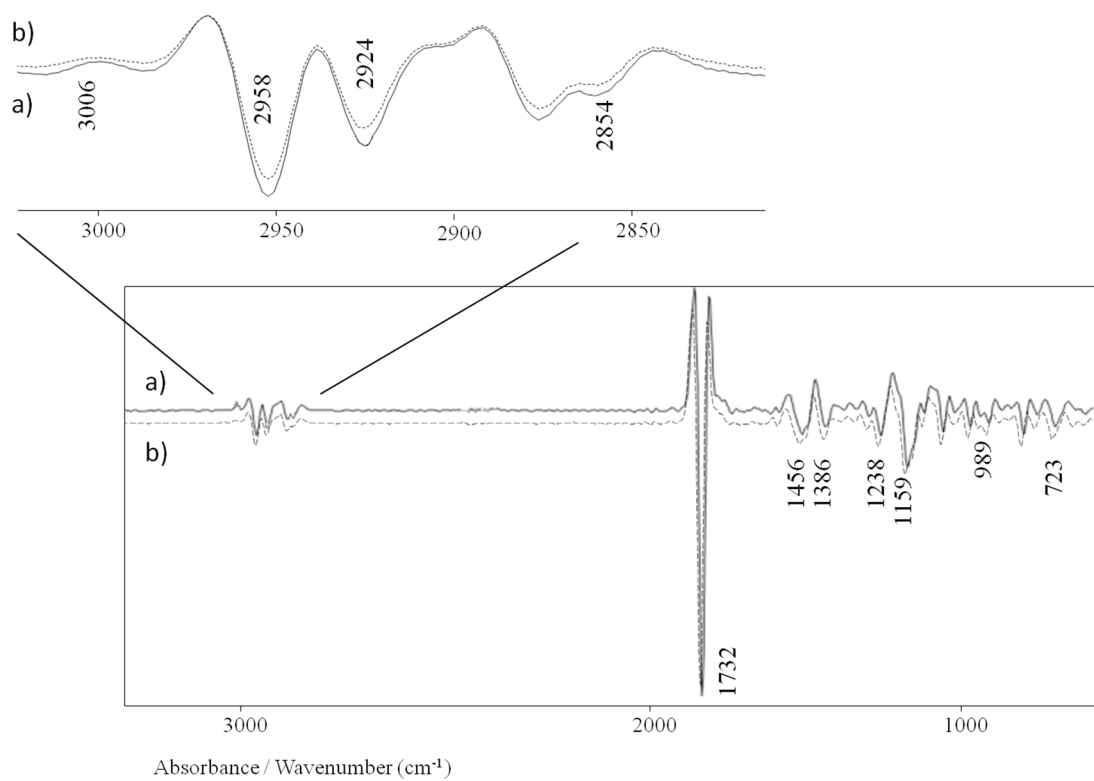**Fig. 4** – Polymeric chain formation and crosslinking by peroxide bond.

Fig. 5 – Second derivative FT-IR spectra and of: a) acrylic latex formulated with AcFAD after one day of drying and b) acrylic latex formulated with AcFAD after five weeks of drying.
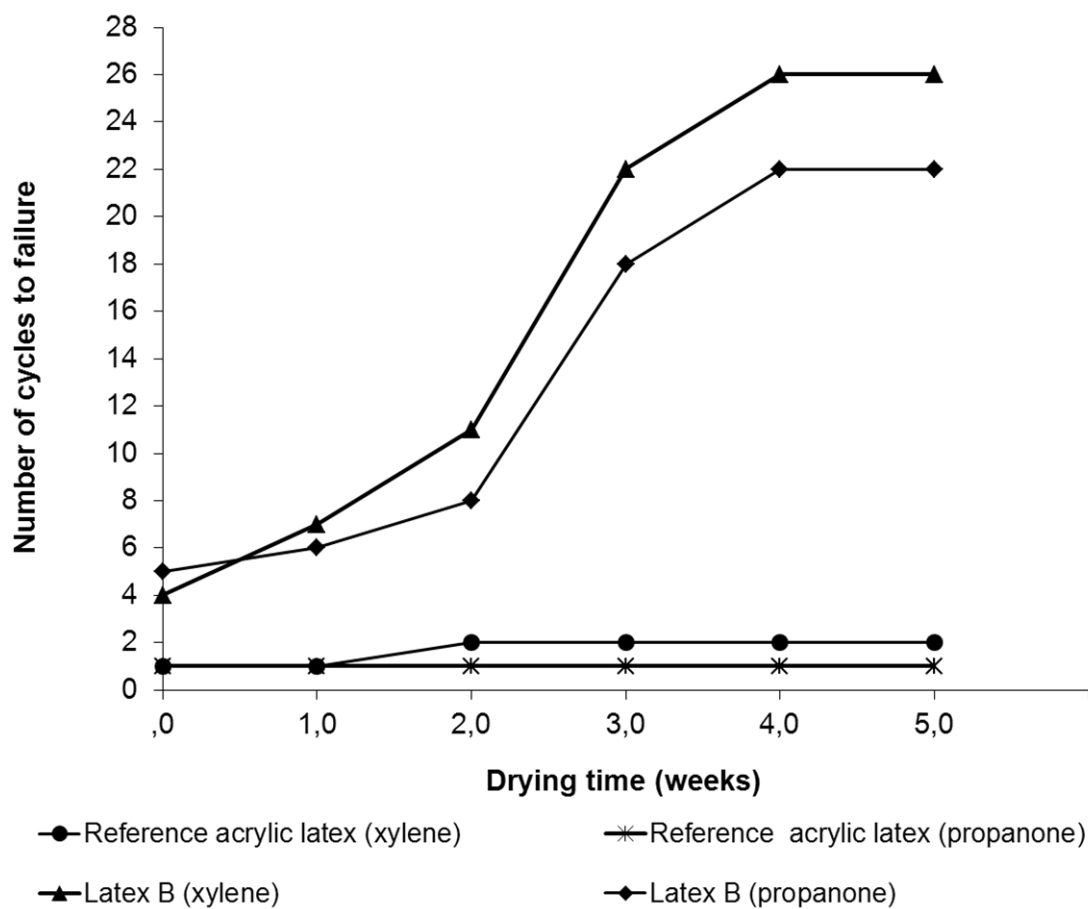
Fig. 6 – Solvent resistance of latex B (copolymerized with AcFAD) and reference acrylic latex, using a) xylene and b) propanone solvents.

Table 1 –Characterization of acrylic emulsion formulations

	Reference emulsion	Emulsion A	Emulsion B
Monomers			
Methyl methacrylate (wt.%)	19.1	14.1	14.1
Butyl acrylate (wt.%)	19.1	14.1	14.1
Acrylic acid (wt.%)	2.3	2.3	2.3
AcFAD (wt.%)	0.0	10	10
Surfactants			
Ethoxylated alkyl sulphate (wt.%)	2.0	2.0	0.0
Dodecyl benzenesulfonic acid sodium salt (wt.%)	0.0	0.0	1.0
Fatty alcohol ether sulfosuccinate disodium salt (FAES) (wt.%)	0.0	0.0	1.0
Others			
Sodium persulfate, additives (biocides, anti-foaming, pH control agent) (wt.%)	1.5	1.5	1.5
Water (wt.%)	56.0	56.0	56.0
Theoretical solid content (%)	44.0	44.0	44.0
Viscosity (mPa·s)	32.5	26.4	59.1
Solids contents (%)	42.6	37.3	42.4
Filtration residue (%)	1.1	2.6	1.3
MFT (ºC)	15.0	6.5	-3.3