Development of monomers for production of high performance paints

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To my son Afonso…

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Abbreviations and symbols

AA – acrylic acid

AC - acryloyl chloride

AcFAD - acrylic fatty acid derivative

AFAD – allyl fatty acid derivative

BA – butyl acrylated

BP - benzoyl peroxide

^{13}C – NMR – carbon 13 nuclear magnetic resonance

CAM – castor acrylated monomer

$CDCl_3$ – deuterated chloroform

CFA - conjugated fatty acids

CLA - conjugated linoleic acid

COSY- correlated spectroscopy

CMC - critical micelle concentration

DBSA - dodecyl benzene sulfonic acid sodium salt

FAAC – intermediate reactive product

FAES – fatty alcohol ether sulfosuccinate disodium sal

DMA - dynamic mechanical analysis

DSC - differential scanning calorimetry

EG - ethylene glycol

FAD – fatty acid derivatives

FAGDE - fatty acid glycol diester

FAGE - fatty acid glycol ester

FAME - fatty acid methyl ester

FID - flame ionization detector

FT-IR – fourier transformed infrared

GC - gas chromatography

GC-MS - gas chromatography–mass spectroscopy

^{1}H-NMR - proton nuclear magnetic resonance

HEMA - (Hydroxyethyl)methacrylate

HLB - hydrophilic – lipophilic balance

HMBC - heteronuclear multiple bond correlation

HSQC - heteronuclear single quantum correlation

IR - infra red

IV – iodine value

KOH – potassium hydroxide

MFT - minimum film-forming temperature

MMA - methyl methacrylate

MS - mass spectroscopy

NaOH – sodium hydroxide

NMR - nuclear magnetic resonance

N_2 - nitrogen

o/w – oil in water

PCl_3 – phosphorous trichloride

pH- potential of hydrogen

PSD - particle size distribution

T_g - glass transition temperature

TG - triglyceride

VOC – volatile organic compound

UV – ultraviolet

w/o – water in oil

Abstract

Due to implementation of the Directive 42/2004/CE that requires a reduction in volatile organic compounds (VOC) emissions, the paint industry made special efforts for developing high performance coatings. The introduction of high amounts of soft monomers in acrylic resins, allow obtaining minimum film-forming temperature (MFT) of approximately 0 ºC. Thus, the paints incorporated with these resins do not require the addition of coalescing agents.

Acrylic resins based in soft polymers have the disadvantage that the applied films lose performance in the application (mechanical properties and chemical resistance). Though, the copolymerization of soft monomers, which are capable of reacting with traditional vinyl or acrylic monomers, increase the mechanical and chemical resistance of the film. The monomers derived from fatty acids with a defined degree of unsaturation, are the most suitable for this application since they can be functionalized by the addition of acrylic, vinyl and styrene functions. If on one hand the aliphatic chain works as plasticizer lowering the glass transition temperature (T_g) and the minimum film formation temperature (MFT), on the other hand, double bonds present in the aliphatic chain lead to oxidative cure. Thus, the formed polymer will have a low T_g and may coalesce without using coalescent agents.

In this study, the use of these compounds derived from fatty acids as reactive coalescing agents was also evaluated. During film formation these agents keep the behavior previously described, remaining in the film, instead of evaporating into the atmosphere during the curing process, minimizing in this way VOC emissions.

The need to develop know-how in this area was the major motivation of this thesis. During the present work two compounds: an allyl fatty acids derivative (AFAD) and an acrylic fatty acids derivative (AcFAD), were prepared and characterized by FT-IR, NMR and GC. After the optimization of the synthesis processes, both its performance as reactive coalescing agents and as comonomers was tested on acrylic resins and in water-based paints. It was also necessary to optimize the resin incorporated with AcFAD formulation, starting from a commercial acrylic resin.

As reactive coalescing agents, it was proved that both have particular interest as non-volatile additives in paints, since when compared to the commercial resin an increase in the T_g, a considerable reduction in MFT and an increase in rubbing resistance test were observed. Thus, and due to the presence of conjugated double bonds, they can be used as auto-oxidative crosslinking agents.

The results obtained for the resins copolymerized with AFAD AcFAD were compared with a commercial acrylic resin. Improvements in the final resins properties were observed. The resin with AcFAD showed better performance than the resin with AFAD, particularly in the film mechanical properties (MFT and rubbing resistance test). In the films produced with AFAD the polymerization mainly occurs by the conjugated double bonds, since the terminal allylic double bond is less reactive. The paints produced with resins incorporating AFAD and AcFAD also demonstrated better performances, namely in the improvement of solvent resistance and decreases in MFT and in through-drying times.

Resumo

Devido à implementação da diretiva 42/2004/CE que obriga a uma diminuição da emissão dos compostos orgânicos voláteis (COV), a indústria das tintas tem procurado desenvolver tecnologias que permitam obter tintas de elevado desempenho. Uma possível forma de consegui-lo é formular resinas com maior quantidade de monómeros macios que permitem obter uma temperatura mínima de formação de filme (TMF) de aproximadamente 0 ºC. Desta forma, as tintas incorporadas com essas resinas não necessitam da adição de agentes coalescentes.

As resinas acrílicas baseadas em polímeros macios têm o inconveniente, de o filme aplicado perder desempenho na aplicação (propriedades mecânicas ou resistência química). A solução passa por copolimerizar monómeros macios, que tenham capacidade de reagir com monómeros acrílicos ou vinílicos tradicionais, aumentando as resistências mecânica e química do filme. Os monómeros derivados de ácidos gordos, com um grau de insaturação definido, são os mais indicados para esta aplicação, já que podem, posteriormente, sofrer reações de funcionalização – por adição de funções acrílicas, vinílicas e estireno. Se por um lado, a cadeia alifática funciona como plastificante, baixando a temperatura de transição vítrea (T_g) e a TMF, por outro, as duplas ligações presentes na cadeia alifática permitem a cura oxidativa. Assim, o polímero formado terá uma baixa T_g, podendo coalescer sem recorrer aos agentes coalescentes.

Neste estudo foi também avaliado o uso destes compostos como coalescentes reativos, isto é, mantêm o comportamento descrito anteriormente, durante a formação de filme, mas em vez de evaporarem para a atmosfera durante o processo de cura, permanecem no filme, diminuindo também a emissão de COV.

A necessidade de desenvolver conhecimento nesta área foi a grande motivação desta tese.

Durante este estudo, foram produzidos e caracterizados por FT-IR, RMN e GC, dois compostos: um derivado de ácidos gordos alílico (AFAD) e outro derivado de ácidos gordos acrílico (AcFAD). Depois de otimizados os processos de síntese, tanto o seu desempenho como coalescentes reativos quer como co-monomeros foi testado em resinas acrílicas e em tintas de base aquosa. Foi também necessário otimizar a formulação da resina com AcFAD, partindo de uma resina acrílica convencional.

Relativamente ao seu desempenho como coalescentes reativos, foi provado que ambos têm especial interesse como aditivos não voláteis em tintas, uma vez que, quando comparados com a resina comercial foi observado um aumento na T_g, uma redução considerável da TMF e um aumento na resistência à esfrega. Assim, devido à presença de duplas ligações conjugadas, podem ser utilizados como agentes reticulantes auto-oxidativos.

Os resultados obtidos para as resinas co-polimerizadas com AFAD e AcFAD foram comparados com os de uma resina comercial, tendo-se verificado uma melhoria nas características finais da resina. A resina com AcFAD obteve melhor desempenho do que a resina com AFAD, nomeadamente nas propriedades mecânicas do filme (TMF e resistência à esfrega). No AFAD a polimerização ocorre maioritariamente pelas duplas ligações conjugadas, já que a dupla terminal alílica é menos reativa. As tintas produzidas com resinas incorporando AFAD e AcFAD também demonstraram melhores resultados, nomeadamente o aumento da resistência ao solvente e uma acentuada diminuição da TMF e dos tempos de secagem em profundidade.

Résume

En raison de la politique mise en œuvre 42/2004/CE qui exige une réduction des émissions de composés organiques volatils (COV), l'industrie de la peinture a cherché à développer des technologies qui permettent d'atteindre les revêtements de haute performance. Une manière possible d'y parvenir est formulée des résines avec plus monomères mous qui peuvent atteindre une température minimale de formation de film (TMF) de l'ordre de 0 °C. Ainsi, les colorants incorporés avec ces résines ne nécessitent pas l'ajout d'agents de coalescence.

Les résines acryliques à base de polymères mous ont l'inconvénient de perdre les performances du film appliqué dans l'application (résistance chimique et propriétés mécaniques). La solution est le copolymérisation de monomères mous, qui sont capables de réagir avec du vinyle ou des monomères acryliques traditionnels, l'augmentation de la résistance mécanique et chimique de la pellicule. Les monomères dérivés d'acides gras ayant un degré d'insaturation définie, sont les plus appropriés pour cette application, une fois qu’ils peuvent ensuite souffrir des réactions de fonctionnalisation. D'une part, la chaîne aliphatiques fonctions comme plastifiant, abaissement de la température de transition vitreuse (T_g) et le TMF, d'autre part, les doubles liaisons présentes dans la chaîne aliphatique permis le oxydatif cure. Ainsi, le polymère formé aura une faible T_g et peuvent fusionner sans utiliser d'agents coalescents.

Dans cette étude, nous avons également évalué l'utilisation de ces composés comme agents de coalescence réactifs, à savoir, qui maintenir le comportement décrit précédemment, dans la formation du film, mais au lieu de s'évaporer dans l'atmosphère pendant le processus de durcissement, restent dans le film, réduisant les émissions COV.

La nécessité de développer une connaissance dans ce domaine a été la motivation principale de cette thèse.

Au cours de cette étude, ont été produits et caractérisé par FT-IR, RMN et GC, deux composés: une dérivée à partir d'acides gras d'allyle (AFAD) et autres dérivés de l'acide gras acrylique (AcFAD). Après avoir optimisé les procédures de synthèse, à la fois sa performance comme agents de coalescence réactifs ou en tant comme co-monomères a été testé sur des résines acryliques et peintures à l'eau. Il est également nécessaire d'optimiser la formulation de la résine AcFAD, à partir d'une résine acrylique classique.

En ce qui concerne sa performance comme agents de coalescence réactifs, il a été prouvé que les deux sont d'un intérêt particulier comme additifs non volatils dans les peintures, par rapport à la résine commerciale était une augmentation de la T_g, une réduction considérable de la TMF et une augmentation de la résistance à l'abrasion. Ainsi, en raison de la présence de doubles liaisons conjuguées, peuvent être utilisés comme agents de réticulation auto-oxydation.

Les résultats obtenus pour les résines co-polymérisées avec le AFAD et AcFAD ont été comparés avec une résine commerciale, et il ya eu des améliorations dans les caractéristiques finales de la résine. La résine avec AcFAD de meilleurs résultats que la résine avec AFAD, en particulier dans les propriétés mécaniques du film (TMF et résistance à l'abrasion). Dans AFAD la polymérisation se fait principalement par des liaisons doubles conjuguées, parce que la double liaison allylique terminale est moins réactif. Les peintures produites avec des résines incorporant AFAD et AcFAD également montré les meilleurs résultats, à savoir l'amélioration de la résistance aux solvants et une diminution marquée de la MFT et le temps de séchage en profondeur.

Chapter 1

CHAPTER 1 - Introduction

In recent years there has been a global awareness towards environment issues, in particular with air quality and therefore the concern with the emission of volatile organic compounds (VOC) into the atmosphere, either by that natural reasons - forests, agro-livestock, etc - or as a result of transport activities, use of household products, use of glues and adhesives, paints and varnishes, etc. These emissions undergo chemical reactions in the atmosphere leading to the formation of photochemical oxidants. The sunlight action on NOx (nitrogen oxides) released by petrol and diesel vehicles and the VOC also released by these vehicles and the other activities previously mentioned, leads to the formation of ozone in troposphere. The ozone formed at this level might reduce the resistance to infection of living organisms, cause eyes irritation and breathing difficulties. By affecting photosynthesis, the ozone can also cause damage to crops reducing yields and cause damage to forests.

Usually high levels of ozone are observed, in calm and sunny days of summer when air is already polluted with nitrogen oxides and VOC. The "photochemical smog" resulting from the reaction of these compounds and the formation of ozone may persist for several days and can be transported over long distances because ozone formation often occurs in areas downwind for the sources of pollution [1].

The European Commission responsible for studying this problem recognized that tropospheric ozone pollution is a widespread and chronic problem in the European Community. Given the cross-border dimension of the tropospheric ozone occurence, the Commission proposed a directive on national emission ceilings, according that the national emissions of sulfur dioxide, nitrogen oxides, volatile organic compounds and ammonia can not exceed certain limits in each Member State, in 2010 [1].

As already mentioned, the use of paints and varnishes contribute to the total emission of VOC. However, these emissions decreased considerably after the implementation of Directive 1999/13/CE, of 11 March 1999 concerning the limitation of VOC in certain activities and installations. This Directive has a direct impact on many sectors of paint industry but not in the decorative paints since these are generally applied to structures and installations in work and not in fixed workshops. Despite, the use of decorative paints contributes to the emission of VOC into the atmosphere and it is calculated that gives rise to about 550,000 tons of emissions, which represents ca. 3 % of total emissions in the European Union. As a consequence the paint industry has been driving many of its research and development efforts to reduce the use of VOC [2]. This includes the gradual discontinuation of painting systems with film-formers that can only be used in paints with high VOC content such as chlorinated rubber, vinyl and acrylic resins soluble in solvents, etc. and the study of new products which satisfy all of the procedures proposed by the European Commission, Directive 1999/13/CE and Directive 2004/42/CE [3] that require the reduction of solvent emissions to the atmosphere and the solvent content of products.

The main options for reducing VOC in decorative paints are:

- substitution of solvent-based products for aqueous products;
- reduction of solvent content in water-based products that already exist;
- reducing the solvent content of solvent based products, when aqueous products do not reach the quality required by consumers.

To reduce solvents in water-based paints it is necessary to develop polymers that allow the formulation of products whose films are formed at room temperature without the need of coalescing agents. These agents are solvents and therefore contribute to increase the emissions of VOC into the atmosphere [4-6]. The knowledge in alkyd resins drying mechanisms allowed the developing of monomers with similar oxidative drying mechanisms. Thus, the polymer would have a low glass transition temperature (T_g) value, allowing it to coalesce without the addition of any coalescing agents.

The monomers derived from fatty acids, with a defined degree of unsaturation, are indicated to this type of application since the fatty acid chain acts as a plasticizer lowering the T_g and hence the minimum film-forming temperature (MFT).

In this study it was given particular attention to coalescing agents and reactive coalescing agents. Coalescing agents are often used to lower the MFT and obtain a uniform film. Indeed, in a first stage, they act as plasticizers and then evaporate into the atmosphere, contributing to increase VOC emissions. Reactive coalescing agents are also responsible for film formation, remaining in the film even after drying and, as consequence, decreasing VOC emissions [7-9]. Some studies referred dicyclopentenyl esters, mono-functional epoxy acrylates and aliphatic epoxides containing polar groups to act as coalescent agents in UV formulations, resins, adhesives [10, 11].

During the last years, there has been a demand for this type of monomers and studies converge to the development of CAM (Castor Acrylated Monomer), a monomer obtain by modification of existing conventional polymers, which allows to obtain paints with desirable characteristics [12, 13].

Several studies have focused on unsaturated vegetable oils functionalization by adding acrylic, vinyl and styrene functions, however its use was proposed in coatings and textile [14, 15]. Besides, there are many studies being conducted on acrylate esters or methacrylate alkenols of long fatty acid chain derivatives, typically involving an esterification reaction of an ethylenically unsaturated carboxylic acid [16].

These studies consider the use of functionalized vegetable oils in coatings and lacquers, as comonomers or polymers, and not as a coalescing or reactive coalescing agents [17, 18].

Thus, the work described in this thesis intended to study the synthesis of monomers with oxidative cure that would allow the production of free VOC paints.

To achieve this, two different compounds derived from conjugated fatty acids, AFAD and AcFAD, were synthesized. These derivatives have characteristics which contribute to reduce VOC, since promote oxidative cure, when used as additives in the paint formulation or as comonomers in the synthesis of the film former polymer emulsion, and consequently improve the performance of paints.

1.1. Vegetable oils

1.1.1. Composition of vegetable oils

Vegetable oils are mainly made of triglycerides, which are three long hydrocarbon chain esters linked to one glycerol molecule. These, also called fatty acids, can be divided into unsaturated or saturated acids, according to the presence or not of double bonds. The degree of unsaturation is characterized by the iodine value (IV) where high IV indicates more unsaturated fatty acids. Fatty acids can also be classified as drying, semi-drying and non-drying according to their ability to dry into a solid film (Table 1.1) [19, 20].

Table 1. 1 - Classification of drying oils according to the iodine value [21].

Oil classification	**Iodine value**
Drying	>150
Semi-drying	100 – 150
Non-drying	<100

Vegetable oils have origin in several sources and the differences are related to the fatty acids chains length and the number, orientation and position of double bonds in the aliphatic chain [22]. Depending on the raw material, different fatty acids can be part of the constitution of vegetable oils; some examples are shown in Table 1.2.

Table 1. 2 – Examples of some unsaturated fatty acids frequently found in vegetable oils.

Fatty acid name	**Chemical structure**	**C x:y** [a)]
Myristoleic acid	$CH_3(CH_2)_3CH=CH(CH_2)_7COOH$	14:1 Δ^{9Z}
Palmitoleic acid	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	16:1 Δ^{9Z}
Sapienic acid	$CH_3(CH_2)_8CH=CH(CH_2)_4COOH$	16:1 Δ^{6Z}
Oleic acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	18:1 Δ^{9Z}
Linoleic acid	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$	18:2 $\Delta^{9Z\text{-}12E}$
Linolenic acid	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$	18:3 $\Delta^{9Z\text{-}12Z\text{-}15Z}$
Erucic acid	$CH_3(CH_2)_7CH=CH(CH_2)_{11}COOH$	22:1 Δ^{13Z}

[a)] x means the number of carbon and y means the number of double bonds.

1.1.2. Synthesis of derivatives from vegetable oils

In the present study, an allyl fatty acid derivative (AFAD) and an acrylic fatty acid derivative (AcFAD), both derived from vegetable oils, were synthesized by two different processes: two-step esterification and transesterification. The two-step esterification was accomplished by two different via; i) the conjugated fatty acid (CFA) was reacted with phosphorous trichloride (PCl_3) forming an intermediate reactive product (FAAC) that was reacted with an alcohol (AA) leading to the final product, AFAD, (Fig. 1.1); ii) the second via considered, the CFA to react with ethylene glycol (EG) followed by esterification with acryloyl chloride (AC) (Fig. 1.1). In both cases the final products are easy to obtain with high conversions and in short reactions time. In oil transesterification, the triglyceride reacts with an alcohol (AA) in the presence of a homogeneous catalyst (usually NaOH or KOH) and an ester (AFAD) and glycerol are formed (Fig. 1.1). The disadvantage of this process is the formation of secondary products, namely soaps that are responsible for the formation of emulsions during the purification process [23, 24].

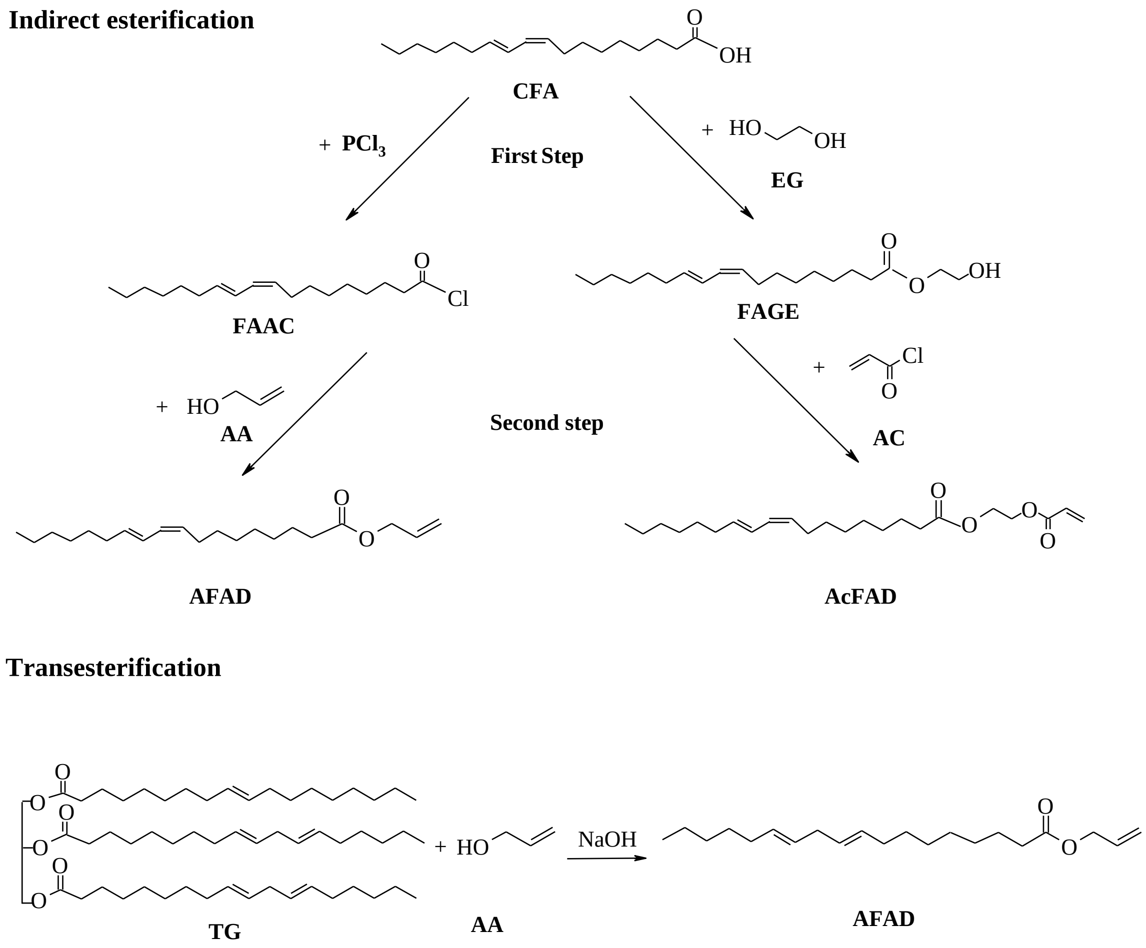


Fig. 1. 1 – Reactions involved in AFAD and AcFAD synthesis process.

1.1.2.1. Oxidative cure

AFAD and AcFAD might be used as additives or comonomers in emulsion or in paints, due to their structural characteristics that are similar to vegetable oils and allow for oxidative cure.

The drying oils process (Fig. 1.2) is a reaction that involves the double bonds of the aliphatic chain and is related to the number of double bonds; oils with higher unsaturations dry faster and if those are conjugated the drying process is even faster [25]. The drying does not occur with water evaporation, although it begins during this process. In fact, during the film drying, when water begins to evaporate, the particles get close each other and coalescence take place – physical drying [25]. After that the molecules are more predisposed for the oxidative cure – chemical drying. In the whole process, this is the most important reaction that takes place - the spontaneously reaction with the atmospheric oxygen. During the oxidative cure process (Fig. 1.3), the allylic hydrogen from the double bond is subtracted and the radical formed ($R^•$) reacts with atmospheric oxygen leading to the formation of hydroperoxides. This happens at the same time the conjugation of double bonds occurs. Then a metal-catalyzed reaction occurs and the hydroperoxides start to decompose in peroxy ($ROO^•$) and alkoxy ($RO^•$) [26-30]. Addition of driers may be necessary to catalyse the decomposition of hydroperoxides allowing the formation of crosslinked hardener films.

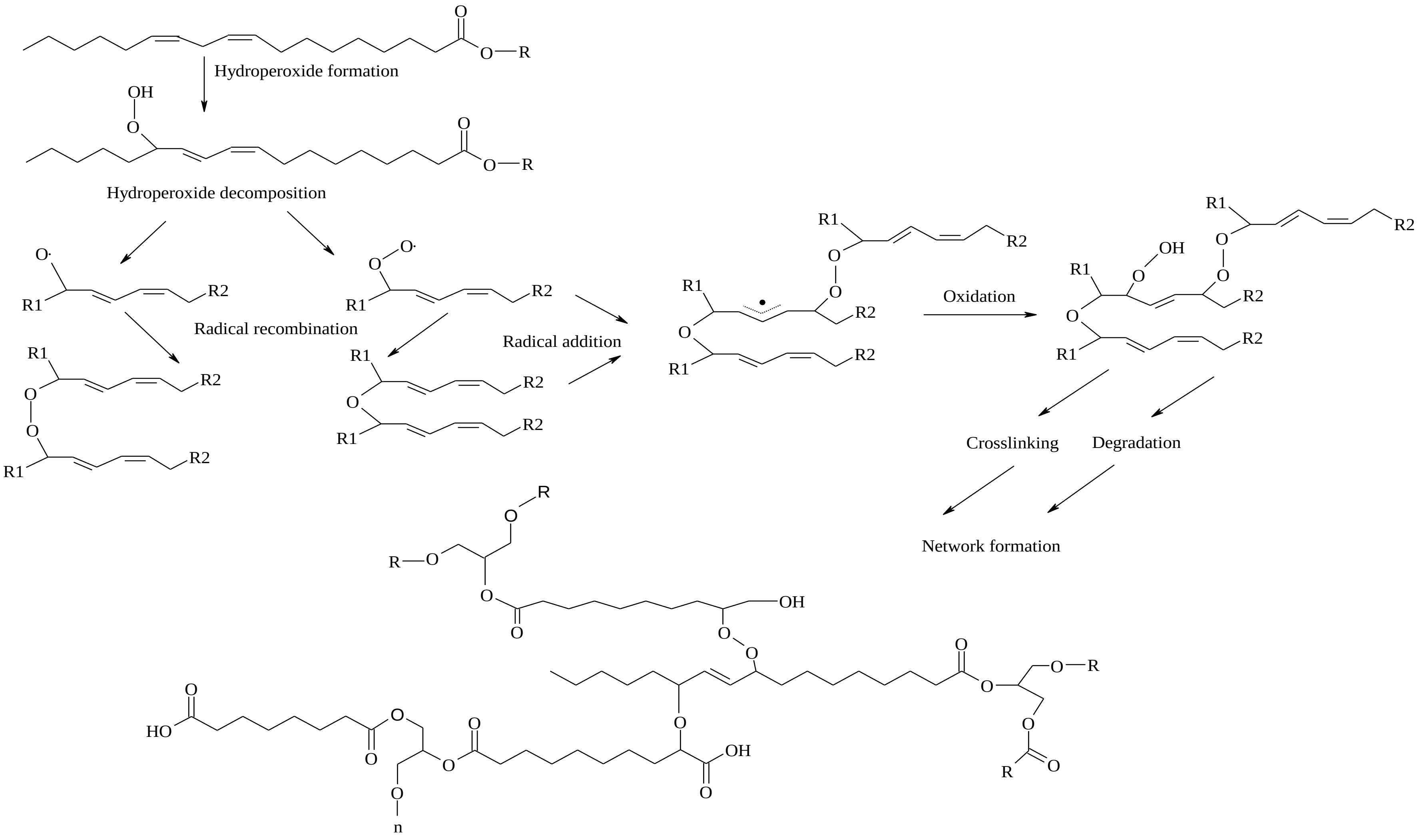


Fig. 1. 2 – Oxidative cure process of unsaturated fatty acid in vegetable oils [31].

Furthermore, these free radical chain reactions occur in three steps; i) initiation; ii) propagation and; iii) termination, generically sketched in Fig. 1.3.

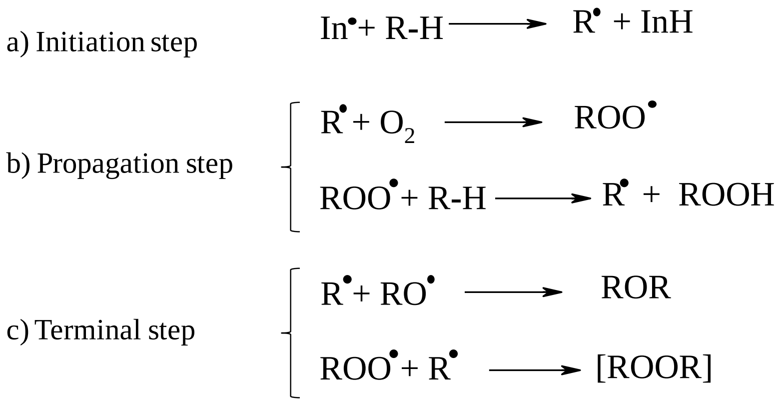


Fig. 1. 3– General radical reactions involved in oxidative cure of vegetable oils derivatives.

In *initiation step* the initiator free radical ($In^{\bullet}$) induces the abstraction of an allylic hydrogen atom from the fatty acid (R-H) leading to the formation of a radical ($R^{\bullet}$) (Fig. 1.3a). This reaction can take place through thermal hydroperoxide decompositions, by the action of driers or via some initiating species on the substrate. During this stage viscosity increases and superficial drying occurs [31].

The *propagation step* involves two reactions (Fig. 1.3b). The first usually starts with the attack of the molecular oxygen to the radical ($R^{\bullet}$), while in the second the peroxy group ($ROO^{\bullet}$) promotes the abstraction of the hydrogen R-H, from another fatty acid chain and another radical ($R^{\bullet}$), and the hydroperoxides species (ROOH) are formed. However, propagation step is not as simple as previously described; usually the steps involved in free radical chain process include radical coupling with oxygen, atom or group transfer, fragmentation, rearrangement and cyclization [31].

The *termination step* occurs by radical recombination to give peroxy, ether or carbon-carbon crosslinking (Fig. 1.3c). These reactions are responsible for the films hardness. Besides, in the presence of conjugated double bonds, radical recombination can lead to the propagation of double bonds to form crosslinked networks. Rearrangement of the double bonds can move the radicals further down the chain. Oxygen can go on to react with the carbon radicals to form peroxy radicals.

1.1.2.2. Driers

Drying oils usually take some time to dry and the addition of catalysts, frequently called driers, might be necessary to accelerate the oxidative cure. Driers are metal soaps of carboxylic groups used as additives materials which contain metals of variable oxidation states. The drying process occurs through a succession of oxidation and reduction reactions.

Usually they are combinations of different metals that are categorized as primary, secondary and auxiliary driers. Primary driers, also known as active or oxidation driers, are able to catalyse the atmospheric oxygen reaction and the decomposition of hydroperoxide to form free radicals, due to variable valencies of metals (Fig. 1.4) [31, 32]. The most common metals of this type are cobalt and manganese. Cobalt, for example, becomes inactive after the fast oxidation step, which leads to a very slow drying of the deeper layers. Cobalt leads to more rapid drying at the surface of the film than in the bulk. The paint surface can wrinkle if it dries faster than the lower layers as the film retracts as it hardens. For this reason, through-driers are added with the cobalt to aid the drying of the bulk of the film. In these cases it is desirable the introduction of secondary driers, also called as through-driers, to improve peroxide decomposition [27]. As the name indicate, they are responsible for drying the deep layers of the film and consequently for the crosslinking. Barium, zirconium and bismuth are the most used metals [33]. Auxiliary driers are responsible for improve the activity of the primary driers, leading to films with better performance and quality. Calcium, zinc and lithium are common used as auxiliary driers. Since the function of this type of driers is not well known, they are often used as secondary driers. The term “auxiliary” should then be discontinued and all the driers that are not categorized as primary driers can be classified as secondary driers.

$$ROOH + M^{n+} \rightleftharpoons [(ROOH)M]^{n+}$$

$$[(ROOH)M]^{n+} \longrightarrow RO\cdot + [M^{(n+1)+}(OH^{-})]^{n+}$$

$$ROOH + M^{(n+1)+} \rightleftharpoons [(ROOH)M]^{(n+1)+}$$

$$[(ROOH)M]^{(n+1)+} \longrightarrow ROO\cdot + M^{n+} + H^{+}$$

$$O_2 + M^{n+} \rightleftharpoons [M^{(n+1)+}(O_2)\cdot^{-})]^{n+}$$

$$[M^{(n+1)+}(O_2)\cdot^{-})]^{n+} + RH \longrightarrow [M^{(n+1)}(OOH^{-})]^{n+} + R\cdot$$

$$[M^{(n+1)+} + RH \longrightarrow M^{n+} + H^{+} + R\cdot$$

Fig. 1. 4– Radical reactions involved in oxidative cure in catalysts presence [31].

Furthermore, the use of driers should be controlled and requires special attention, namely zirconium and manganese might change the desired colour while cobalt and calcium can lead to premature drying which can reduce oxygen diffusion to the deeper layers leading to the formation of wrinkling [32].

1.2. Polymerization

The aim of the present study was to use allyl fatty acid derivative (AFAD) and acrylic fatty acid derivative (AcFAD) not only as a paint additive, but also as a comonomer in radical polymerization.

In the free radical polymerization mechanism, the monomers are added to a terminal reactive site, usually called active center, increasing the polymeric chain. As a result of the addition of each monomer, the active center is transferred to the end of the chain newly created. This process can be divided in three steps: initiation, propagation and termination [34].

The *initiation step* can occur spontaneously by heat absorption or UV light, but typically occurs when small amounts of initiators (In-In) are added. These are organic compounds capable to be thermally decomposed forming free radicals and the most common are peroxide and azo compounds. The free radicals are very reactive and have unpaired electrons. The reaction involves two steps: first, in presence of monomers, the initiator decomposes into free radicals (Fig. 1.5a) and then the radical addition to the monomer takes place (Fig. 1.5b) [35].

During propagation step, the polymeric chains grow by quick addition of the monomer to the active center, i.e., the free radical attacks the monomer double bond and another radical is formed (Fig. 1.5c). This step stops when the termination reaction starts [35, 36].

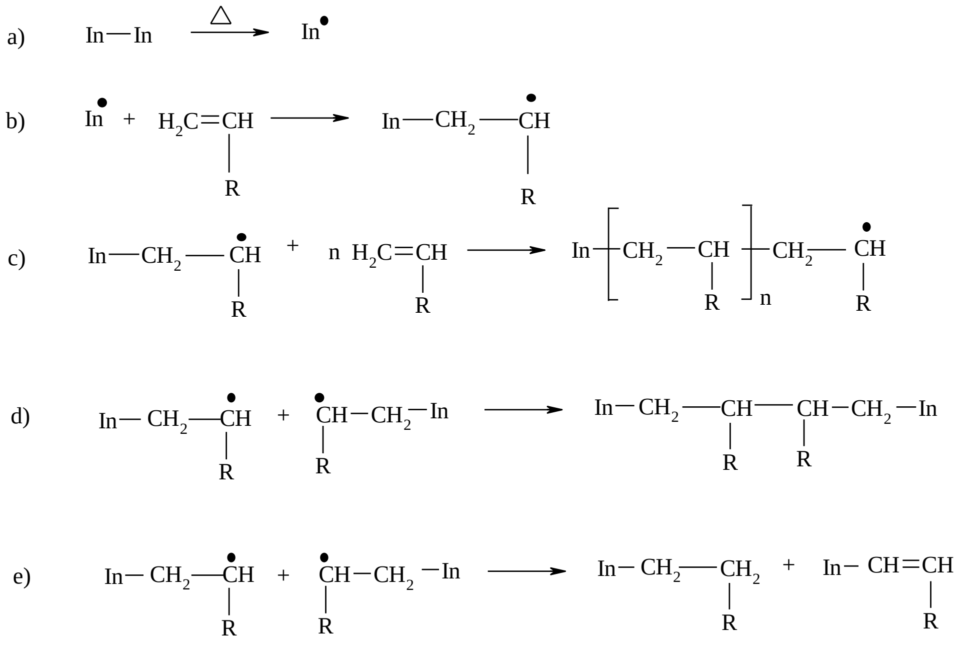


Fig. 1. 5– Reactions involved in free radical polymerization (In represents the initiator and R represents a monomers).

Termination step can occur by combination (Fig. 1.5d) or disproportionation reactions (Fig. 1.5e). In combination, two growing polymer chains react forming a single molecule, while in disproportionation – a less common process - a hydrogen atom is moved from one radical to another and a double bond is formed in one polymeric chain [36].

1.2.1. Solvent polymerization

In this particular polymerization process the monomer is dissolved in a non-reactive solvent in the presence of a catalyst and all reagents are in the same phase.

The degree of polymerization is also affected by the solvent, which reduces the viscosity of the system. The low monomer concentration causes a decrease in the rate and in polymerization degree.

In conventional free radical polymerization is difficult to control the polymer chain length but solvent polymerization can be used to prepare polymers with low molecular weight. The molecular weight of polymers can be controlled by the addition of a chain transfer agent to the solvent, i.e., chain transfer agents can control the termination process (usually mercaptans are used). This is very important since some of the mechanical and physical polymers properties depend on the chain length [36].

To obtain pure polymer, it is necessary to remove the solvent, which implies precipitation and separation of the polymer. Therefore, this type of polymerization is often used when a polymer in solution is desired [35].

1.2.2. Emulsion polymerization

Emulsions are unstable systems with two liquid phases, where small droplets are dispersed into another liquid present in excess, named continuous phase [37, 38]. However, when stirring is stopped and if the dispersed droplets are not charged – unstable emulsion - emulsion starts to collapse. This occurs due to the creaming, aggregation and coalescence of particles. To make an emulsion stable, it is necessary to decrease the dispersed particles size, to reduce the dispersion density difference and to protect the surface of oil droplets.

Commonly, emulsions are composed of water (polar phase) and oil (non-polar phase) and can be classified as oil in water (o/w) or water in oil (w/o). In the first case, oil phase is dispersed as droplets in an aqueous continuous phase; in the other case, are water droplets that are dispersed in the oil phase. On the other hand, if water is yet dispersed in oil droplets that are in turn dispersed in water or if the oil is dispersed in water droplets which are dispersed in oil, the expression multiple-phase emulsions is indicated [37].

The emulsion type is formed according to the stability of the surfactant layer that involves the droplets. If a water-stable layer is formed around the oils droplets an o/w emulsion is formed, whereas if an oil-stable layer is formed around the water droplets a w/o emulsion is formed.

Therefore, to obtain stable emulsions, it is necessary to select the surfactants. When two liquids are immiscible, surfactant molecules will stabilize the droplets of one liquid in the other [39]. Further, if the oil droplets coalesce faster than the water droplets, a w/o system is formed, therefore the rate that droplets coalesce is decisive. Besides, in a w/o emulsion, hydrocarbon chains protect the water droplets from coalescing [37].

During the emulsion polymerization, the monomers must be emulsified in a continuous aqueous phase and stabilized by a surfactant (Fig. 1.6a). A water soluble free radical initiator ($R^{\cdot}$) is added to start the polymerization (Fig. 1.6b).

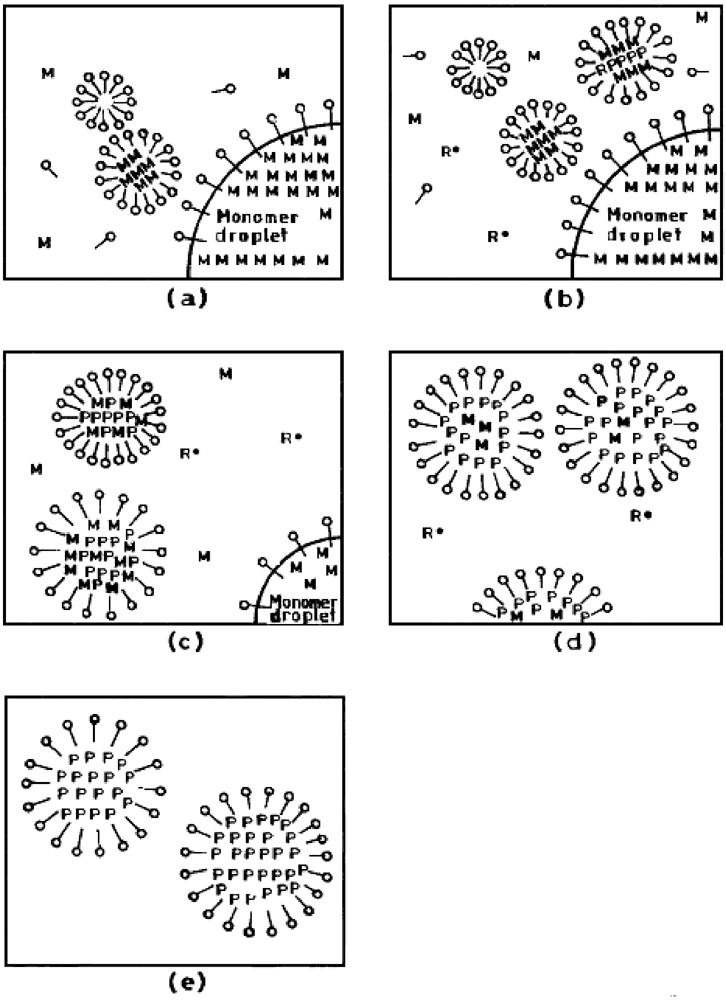


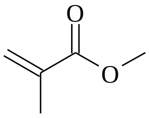
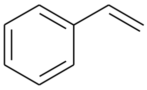
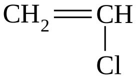
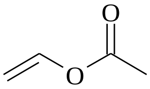
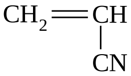
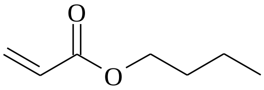
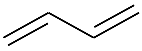
Fig. 1. 6– Emulsion polymerization scheme (—O represents an emulsifier molecule, M a monomer molecule, P a polymer molecule and R a free radical [36].

Polymerization process can be divided into three distinct stages. The first one is the initial stage where the monomer (M) reacts with free radicals ($R^{\cdot}$) and the monomer diffuses to the micelles from the droplets beginning the polymerization into the micelles, leading to the formation of polymer particles (Fig. 1.6b, c). In the second one, the polymerization occurs only in monomer-swollen polymer particles by diffusion of monomer from droplets [36]. All the emulsified micelles disappear and the surfactant is no longer available to form new particles (Fig. 1.6c). The last stage starts when monomer droplets disappear and finishes when the monomers in the particles and in the water phase are exhausted (Fig. 1.6d, e) [37, 40-42].

The obtained product - latex - is a colloidal dispersion of polymer particles, usually with particle sizes between 50–300 nm. Particle size is influenced by the surfactant concentration – high concentration leads to small particles sizes and agitation conditions [38].

Acrylates, styrene, vinyl chloride and vinyl acetate are some of the monomers that can be copolymerized by emulsion polymerization. These comonomers are usually used in combinations of hard and soft monomers (Table 1.3). The combination of different functional monomers allows obtaining polymers with certain adhesion, cohesion and crosslinking properties.

Table 1. 3 – Hard and soft monomers.

Hard monomers	**Name**	**Structure**
	Methyl methacrylate	
	Styrene	
	Vinyl chloride	 $CH_2=\underset{\underset{Cl}{\vert}}{CH}$
	Vinyl acetate	
	Acrylonitrile	 $CH_2=\underset{\underset{CN}{\vert}}{CH}$
Soft monomers		
	Butyl acrylate	
	Ethylene	$CH_2=CH_2$
	Butadiene	

Efficient heat transfer (due to the low viscosity of the continuous phase), higher monomer consumption and fast polymerization rates are great advantages of emulsion polymerization, wherein the polymer can be recovered by film formation or coagulation [35, 42]. On other hand, the polymer contamination with surfactants and additives is one disadvantage [42, 43].

1.2.2.1. Reactants for free radical emulsion polymerization

An emulsion is constituted by a continuous phase (usually water), monomers, initiator, surfactants, salts, pH controllers and chain transfers agents.

The monomers are usually insoluble or sparingly soluble in water and polymerizable by free radical mechanism. The most common are acrylates and methacrylates, acrylic acid, styrene, vinyl acetate and vinyl chloride. The initiator must be soluble in water; the most common are sodium, potassium and ammonia persulfate salts. Redox systems might be used when polymerizations require low temperatures (<50 ºC). High concentrations of initiator can increase the number of instability particles in the aqueous phase [44]

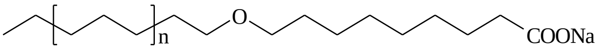
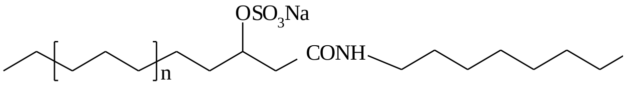
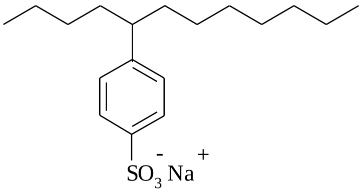
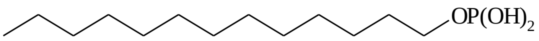
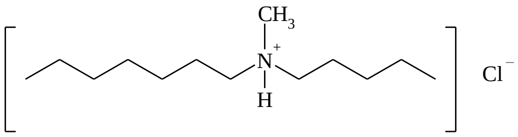
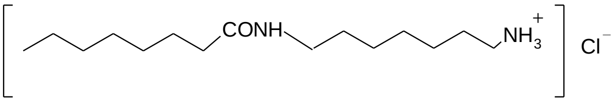
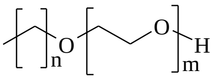
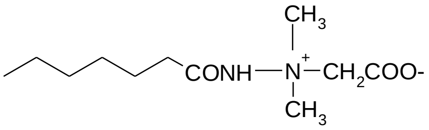
The surfactants are added in small quantities (usually 1 – 1.5 %) and are responsible for monomers droplets stabilization, micelles formation and for the developing polymer particles stabilization. They are classified according to the hydrophilic group [40]. The most common in emulsion polymerization are the anionics which are low solubility in water, due to their hydrophobic tails, leading to the formation of micelles.

1.2.2.2. Importance of the surfactant

Surfactants are responsible for the emulsion stability, improving kinetic stability, during the polymerization and the shelf life of the resin [45]. These are molecules with two different portions, usually called “head” and “tail” that differ in polarity and in solubility. Depending on the basis of the polar head group can be divided as anionics, cationics, non-ionics and zwitterionics (or amphoteric) (Table 1.4).

Anionic surfactants are the mostly used and the largest existing class. The hydrophilic polar groups are carboxylate, sulphate, sulfonate and phosphate. The counterions mostly used are sodium and potassium – provide water solubility - and calcium and magnesium – confer oil solubility [46]. Usually, they are incompatible with cationic surfactants (there are some exceptions) and sensitive to hard water.

Table 1. 4– Some examples of anionics, cationics, non-ionics and zwitterionics surfactants used in emulsions [40].

Surfactant type	Surfactant name	Structure example
Anionics		
	Alkoxycarboxylates	
	Sulfated fatty acid amides	
	Sodium dodecylbenzenesulfonate	
	Phosphates of alcohols, phenols or their polyglycol ethers	
Cationics		
	Quarternary alkyl ammonium salts	
	Quaternary amidoamino compounds	
Non-ionics		
	Ethoxylated alcohols	
Zwitterionics		
	Substituted betaines and sulfobetaines	

The most common *cationic surfactants* are the quaternary ammonium and amine based compounds. The first ones are not sensitive to pH and the second ones only act as surfactants in the protonated state. Usually they are stable to pH changes and are compatible with non-ionic surfactants, but incompatible with most anionic surfactants. When, they have only one alkyl group, cationic surfactants are generally soluble in water. Their principal application is the surface modification since they adsorb to must surfaces [47].

Non-ionic surfactants are usually ethoxylated compounds, exhibiting very sensitive temperature physicochemical properties - with high temperatures they became more hydrophobic, i.e. less water soluble. Usually they are compatible with other classes of surfactants and are not sensitive to water. Electrolytes do not affect their physicochemical properties [47].

Zwiterionic surfactants are the smallest surfactants class and comprise both anionic and cationic charge. The most common zwiterionic surfactants are the *N*-alkyl betaines. Depending on pH solution, this surfactant can obtain positive charges in acid solutions – behaving as cationic surfactant, or negative charge in alkaline solutions, behaving as an anionic surfactant. Zwitterionic surfactants are not sensitive to water and are compatible with all the other groups of surfactants, forming mixed micelles [40].

Another possibility is combinations of surfactants and emulsions are prepared to use combination of different surfactants types, generally with different hydrophilic – lipophilic balance (HLB) values. The HLB concept was introduced by Griffin [48, 49] and is only applicable for non-ionics surfactants. Later, Davies [50] introduced a method for determining the HLB value by the contribution composition groups.

O/w emulsions are favoured by hydrophilic surfactants with high HLB. On the other hand, hydrophobic surfactants with low HLB are more appropriate to prepare w/o emulsions.

Obviously, the selection of surfactants should not be made only on the basis of HLB value. First of all, an oil soluble surfactant usually forms w/o emulsions, and water soluble surfactants form o/w emulsions. In addition, surfactants should have tendency to migrate for the oil-water interface. Finally, it is important to note that the combination of surfactants with different HLB values, usually lead to emulsions with the most appropriate characteristics [40].

Furthermore, surfactants with high molecular weight have tendency to be more hydrophobic, leading to higher solubility in a polymeric film [51].

To complete this section, it is important to note that surfactants can also have negative effects. After film formation, surfactants can migrate through the surface affecting some surface properties, such as gloss and water sensitivity [47]. Furthermore they can lixiviate and cause environmental problems. One promising way to resolve that is the use of reactive surfactants, which are chemical bonded to the polymer preventing their migration to the film surface [47].

1.2.2.3. Emulsions characterization

Many techniques to characterize resins produced by emulsion polymerization are available, namely:

- *FTIR (Fourier Transform Infrared) (IR)* which allows characterizing the functional groups present in emulsions and following their progress throughout the reaction;

- *NMR (Nuclear Magnetic Resonance)* allows identifying the structure of the polymer;

- *MFT (minimum film-forming temperature)* is an essential parameter to determine the lower temperature from which the polymer can form a coherent film. It is a measure that depends on the monomer composition and the amount of plasticizer present in the emulsion;

- *DMA (Dynamic Mechanical Analysis),* enables to study the viscoelastic properties, allowing obtain the glass transition temperature;

- *DSC (Differential Scanning Calorimetry),* yields information about physical and chemical changes that involve endothermic or exothermic reactions. In the current work DSC was used to measure the glass transition temperature.

- *Solids contents,* is an important parameter, because it enables control the polymerization, since it allows quantifying the polymer dispersion. When solids content value is low there is a strong indication that some unreacted monomer is present;

- *Particle size distribution (PSD),* is another important parameter that affects the film forming properties of the resin;

- *Viscosity,* is one of the relevant parameters since it influences the latex applicability in the final product. Although it does not depend on the polymer molecular weight it is directly associated to the type of emulsifier system used and the particle size.

1.3. Paints

A paint or coating film is a product based on organic or inorganic binders, which when applied to a substrate produces a cohesive, protective and possibly decorative film [21]; a paint is constituted by a solid and a liquid phases. After applying the paint film, the volatile compounds start to evaporate and a solid and opaque film is formed. In fact, the film formation process in waterborne paints occurs upon evaporation of water and subsequent coalescence of the binder particles. [52, 53]. This process is sketched in figure (1.7).

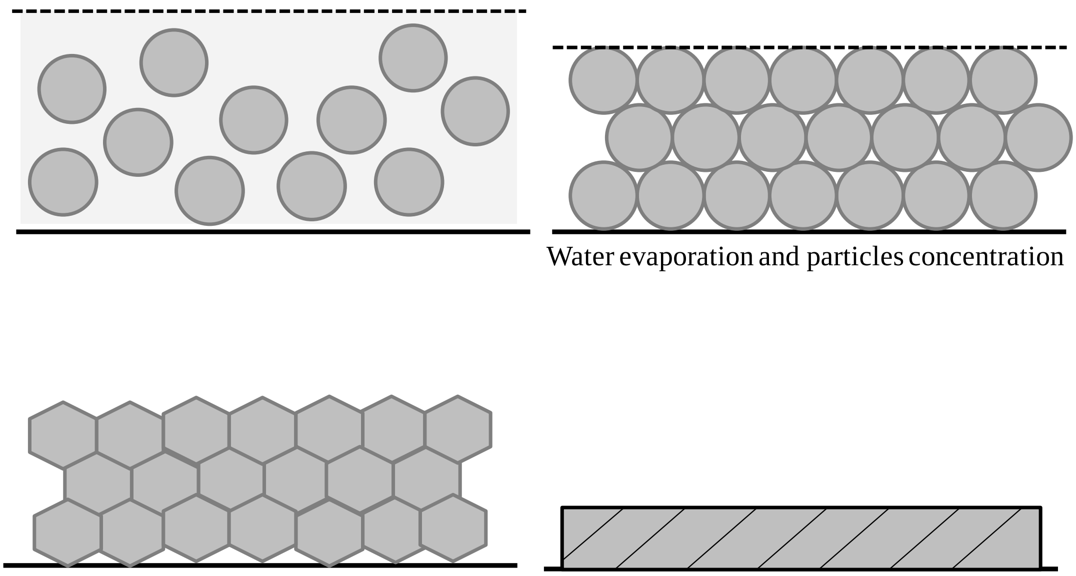


Fig. 1. 7– Coalescence film forming process.

Paints result from the mixture of several compounds whose order of addition is relevant to the paint final properties. The main functions of paints are to protect and to decorate the substrate. A paint to be classified as decorative paint should have the following characteristics: appropriate gloss level, colour and hiding power (optical properties), excellent applicability and levelling (roller or brush marks should disappear shortly after the application) [54].

Paint components include: pigments, fillers, film-formers, solvents/dispersants, volatile and non volatile additives [54].

Pigments are fine solid particles, stable, non-toxic and insoluble in vehicle and solvents, usually they comprise 65-85 % of the weight paint. The hiding power is influenced depending if they are white (very low light is absorbed), black (light is completely absorbed) or coloured (light is selectively absorbed, reflecting complementary light). Pigments have decorative and protective functions, but above all they are responsible for conferring opacity and colour, gloss, environment resistance, improve film adhesion and afford strength to the film. Both chemical composition and physical properties, as crystalline structure and crystals shape and size, have influence on paint properties such as, gloss, colour intensity, transparency and hiding power [21].

Chemically, they can be classified as oxides (TiO_2, ZnO), oxides hydroxides (iron and chromium oxide pigments) and sulphides (ZnS).

Fillers are responsible for increasing solids volume and improve some characteristics. They have low refractive index, thus not contributing significantly to film opacity. Although they are frequently confused with pigments, the major difference is the particle size, which is higher for the fillers [21]. Do the connection between the pigments, ensuring the cohesion of the paint and are often used due to the paint costs reduction.

The amount and type of filler also influence the elasticity, chemical resistance, gloss, rheology, blocking and environmental resistance. Carbonates (calcite and aragonite), silicates (talc, mica and kaolin) and sulphates (barium sulphate) are some examples of fillers.

Film-formers, often called *binders*, are responsible for the formation of a solid film and for inlay the pigments and fillers [21]. These are non-volatile high molecular weight polymers, of synthetic or natural origin, like polyester, epoxy, polyurethanes or, alkyd, acrylic, vinyl-acrylics resins. These are responsible for mechanical and chemical properties of the coating film, like adherence to the substrate and durability, flexibility, toughness, gloss and waterproofness to the film.

Additives are added to the paint in small quantities, and mostly intend to improve film final appearance. According to their function in paints, there are different types of additives and some examples are shown in Table 1.5 [21].

Table 1. 5– Some examples of paints additives and functions.

Additive	Function/ Prevent changes on	Examples
Catalysts (driers)	Accelerate crosslinking reactions	Metal salts (such Co, Mn, Zr, Ca and Ba) of natural organic acids
Dispersants	Gloss, power binder and stability	Polyphosphates
Thickeners	Paint rheology and applicability (for example, prevent pigments and fillers settling during storage)	Cellulose derivatives, acrylic copolymers polyurethanes and inorganics thickeners
Flatting agents	Gloss and transparency	Silicon dioxide and polyethylene waxes
Coalescing agents	Good film formation, evaporate during film drying	Diesters, Glycols, hydrocarbon (white spirit)
Reactive coalescing agents	Good film formation, remain in the film after drying	Fatty acids derivatives
Anti-foaming	Eliminate foam formation, by decreasing surface tension	Silicones, mineral oils and organics
Anti-skinning	Prevent skin formation during storage	Ketoximes, aldoximes and substituted phenols
Biocides	Prevent the development of bacteria, fungi and algae	isothiazolinone and imidazolcarbamate derivatives, formaldehyde
Flow control agents	Wetting of the substrate	Acrylate copolymers
pH control agents	Influence the latex, thickeners and dispersants properties	NaOH, KOH, ammonia and amines
Light stabilisers	Gloss, yellowing, cracking and blistering	HALS and hydroperoxide decomposer

Solvents (or thinners), which are capable of dissolving the paint film-formers reducing its viscosity and facilitating its application. The solvents have influence on film appearance defects, adhesion to the substrate and anti-corrosive effect [21]. They also can increase elasticity and influence the drying.

Dispersants does not dissolve the film-formers, but remain in a fine dispersion. Improve paint applicability.

1.4. Dissertation outline

The thesis is divided into six main chapters: chapter 1 presents an introduction and covers the objective and scope of the work.

Chapter 2 reports the synthesis and characterization of allyl fatty acid derivative (AFAD) and its use as reactive coalescing agent in latexes. The synthesis was done by two different processes and evaluated by FT-IR and NMR. The potential of AFAD as reactive coalescing agent in a reference acrylic emulsion was characterized by measuring the minimum film-forming temperature (MFT), the glass transition temperature (T_g), drying time and evaluating rubbing resistance to solvents.

Chapter 3 describes the synthesis and characterization of a novel acrylic reactive coalescing agent, derived from vegetable oils and their use in resins. The acrylic fatty acid derivative (AcFAD) was synthesized by esterification, which was monitored by the acid value and FT-IR spectroscopy and was characterized by GC–MS and NMR. The behaviour of a standard acrylic emulsion added with AcFAD was characterized by measuring the drying times, minimum film-forming temperatures and solvent rubbing resistance.

Chapter 4 comprises the AcFAD polymerization in solution and in emulsion. Initially, the homo-polymerization of AcFAD, its co-polymerization with MMA and polymers characterization are described. Then, an emulsion based on a commercial acrylic formulation and incorporating the monomer AcFAD was synthesized. As the AcFAD was not efficiently co-polymerized with the other monomers it was necessary to optimize the emulsion formulation.

Chapter 5 includes the synthesis of latexes copolimerized with AFAD and AcFAD. Viscosity, pH, solid content, MFT, zeta potential, gel content and rubbing resistance test were evaluated. High gloss VOC free acrylic paints incorporating those latexes were produced and compared with paints mixed with 5 wt.% of AFAD and AcFAD. The aim was to understand the behavioural differences between AFAD and AcFAD as comonomers and as reactive coalescing agents.

Finally, chapter 6 summarizes the main conclusions of this work and some suggestions for future work.

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Chapter 2

CHAPTER 2 - 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, 1H and 13C 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

2.1. 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 nondrying 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 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 wellknown process, with well-determined molar ratios, reaction times and temperatures [18, 19]. Therefore, AFAD synthesis was also attempted by this process.

2.2. Experimental

2.2.1. 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 benzene 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).

2.2.2. 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.

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

Gas chromatography-flame ionization detection (GC-FID) was performed in a Chrompack CP-9001 coupled with a FID system and equipped with a CP-SiL 88 Column (50 m x 0.25 mm). Helium was used as carrier gas at an internal pressure of 110 kPa. The following operating conditions were used: injector temperature was set at 250 ºC while the detector temperature was set at 270 ºC; the initial temperature of the column, 140 ºC, was maintained for 5 min, and was subsequently increased to 220 ºC at 10 ºC/min. 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 FAMEs (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 quadropule inert mass selective detector 5973N - Agilent with electron impact ionization chamber. GC separation was performed on DB-5MS J&W capillary column (30 m x 0.25 mm I.D., 0.25 µm film thickness). Helium was used as carrier gas with a constant flow of 1 ml/min. The injection was made in split mode (40:1) at 250 ºC. 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 ºC at 3 ºC min^{-1} for 13 min. The MS transfer line temperature was held at 280 °C. Mass spectrometric parameters were set as follows: electron impact ionization with 70 eV energy; ion source temperature, 230 ºC and MS quadrupole temperature, 150 ºC. The MS system was routinely set in full scan mode. 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 ºC, at a heating rate of 10 $ºC\cdot min^{-1}$, 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 ºC were determined by applying 100 µm wet thickness films on 10 x 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.

2.2.3. AFAD Synthesis

2.2.3.1. 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 is 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 benzene and distilled water, until a neutral pH was achieved. The organic layer was dried overnight with anhydrous magnesium sulphate and filtered. Finally the solvent was removed under 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 3400 and

2400 (OH stretching), 2920 and 2855 cm^{-1} (saturated $[(CH_2)_n]$ stretching), 1700 (C=O stretching), 1465 and 1378 (CH_2, CH_3 bending), 1295, 1230 (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, $-C\underline{H_2}-CH_2-C(=O)-$, H_{-3}), 2.35 (*t*, *J*=7.2, 2H, $-CH_2-C(=O)-$, H_{-2}), 11.30 (*brs*, O*H*). **^{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}): 3088 (unsaturated CH_2 anti symmetric stretching), 3005 (CH unsaturated stretching), 2920 and 2855 (saturated $[(CH_2)_n]$ stretching), 1740 (C=O stretching), 1650 (C=C stretching), 1465 and 1378 (CH_2, CH_3 bending), 1173 (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, $-C\underline{H_2}-CH_2-C(=O)-$, 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).

2.2.3.2. AFAD from conjugated fatty acids by two step esterification

The conjugated fatty acids (CFA) mixture composition is shown in Table 2.1. 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 hour. The reaction product was cooled to 10 °C and allylic alcohol (102 g, 1.75 mol) was added dropwise for 45 min. The reaction was continued for 1 hour to guarantee maximum production of AFAD (yield 76 %). Both reactions were monitored via FT-IR.

Table 2. 1- Composition of fatty acid methyl esters (FAME) and allyl fatty acid derivative (AFAD) from conjugated fatty acids (CFA).

% relative	FAME from CFA Composition (%)	AFAD from CFA Composition (%)
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

The purification process was made following the procedure described above. *Conjugated Fatty Acids (CFA)*: **IR** (cm^{-1}): between 3400 and 2400 (OH stretching), 3009 (CH unsaturated stretching), 2920 and 2855 cm^{-1} (saturated $[(CH_2)_n]$ stretching), 1711 (C=O stretching), 1654 (C=C stretching), 1465 and 1378 (CH_2, CH_3 bending), 1173 (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, $-C\underline{H_2}-CH_2-C(=O)-$, 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*, O*H*). **^{13}C NMR** (C18:2 Δ^{9Z-11E},

$CDCl_3$): δ in ppm= 13.91 (-*C*H_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}): 3088 (unsaturated CH_2 anti symmetric stretching), 3009 (CH unsaturated stretching), 2920 and 2855 cm^{-1} (saturated [$(CH_2)_n$] stretching), 1741 (C=O stretching), 1650 (C=C stretching), 1465 and 1378 (CH_2, CH_3 bending), 1173 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, -C$H_{\underline{2}}$-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=C*H*-, $H_{-2'}$), and 5.95 (*dd*, *J*=15.0 and 11.0 Hz, H_{-11}). **^{13}C NMR** ($CDCl_3$): δ in ppm= 13.67 (-*C*H_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-*C*H_2O-, $C_{-1'}$), 125.00-135.00 (C_{-9}-C_{-12}), 117.25 (*C*H_2=CH-, $C_{-3'}$), 132.11 (CH_2=*C*H-, $C_{-2'}$), 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).

2.2.3.3. AFAD from soybean oil by transesterification

Soybean oil (10 g, 11 mmol) was placed into a three necked round bottom flask, equipped with water condenser, thermometer and, magnetic stirrer, and was heated to 65 ºC. 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 settling to ensure separation of the two phases. The purification process was made following the procedure described above. *Soybean oil*: IR (cm^{-1}): 3009 (CH unsaturated stretching), 2926 and 2855 cm^{-1} (saturated [$(CH_2)_n$] stretching), 1746 (C=O stretching), 1654 (C=C stretching), 1461 and 1374 (CH_2, CH_3 bending), 1237, 1164 cm^{-1} (C-O, stretching), 1100, 969 and 914 ($CH=CH_2$, out-of-plane deformation), 722 (CH_2, rocking). *Allyl*

Fatty Acid Derivatives from soybean oil: **IR** (cm^{-1}): 3085 (unsaturated CH_2 anti symmetric stretching), 3009 (CH unsaturated stretching), 2927 and 2856 cm^{-1} (saturated $[(CH_2)_n]$ stretching), 1741 (CH_2=CH-CH_2-OCO-), 1651 (C=C stretching), 1461 and 1377 (CH_2, CH_3 bending), 1238, 1171 (C-O, stretching), 990 and 928 (CH=CH_2, out-of-plane deformation), 722 (CH_2, rocking).

2.3. Results and Discussion

2.3.1. Synthesis Monitoring

The AFAD from palmitic acid (allyl palmitate) (n = 14) were prepared by a two-step esterification (Fig. 2.1) and characterised 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.

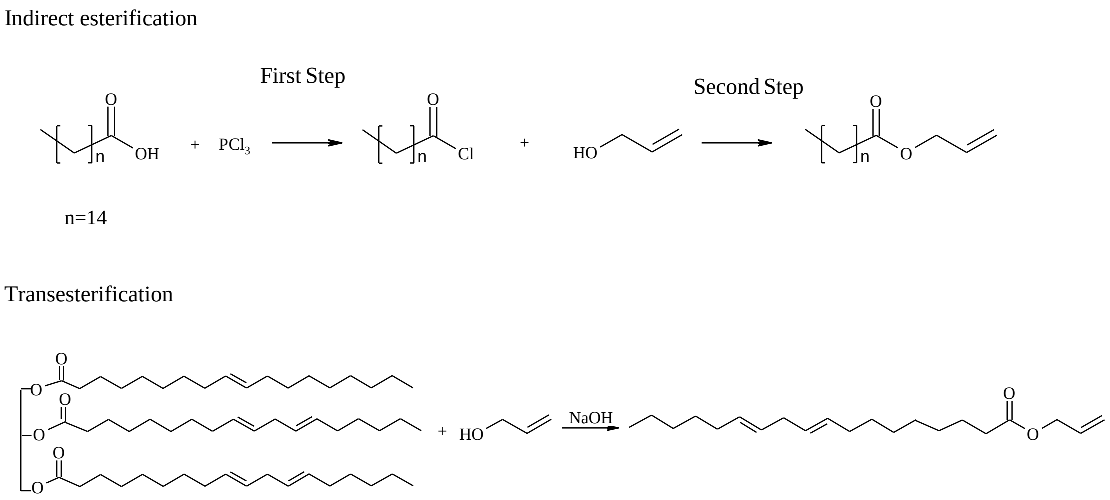

Fig. 2. 1- General scheme of the reactions involved in the AFAD synthesis process.

The disappearance of the broad band corresponding to OH stretching (3400-2400 cm^{-1}) in carboxylic acid groups and the shift of carbonyl band of palmitic acid from 1700 to 1740 cm^{-1}, corresponding to the formation of the ester carbonyl group (C=O stretching vibration) in AFAD are shown in Fig. 2.2e and 2.2f.

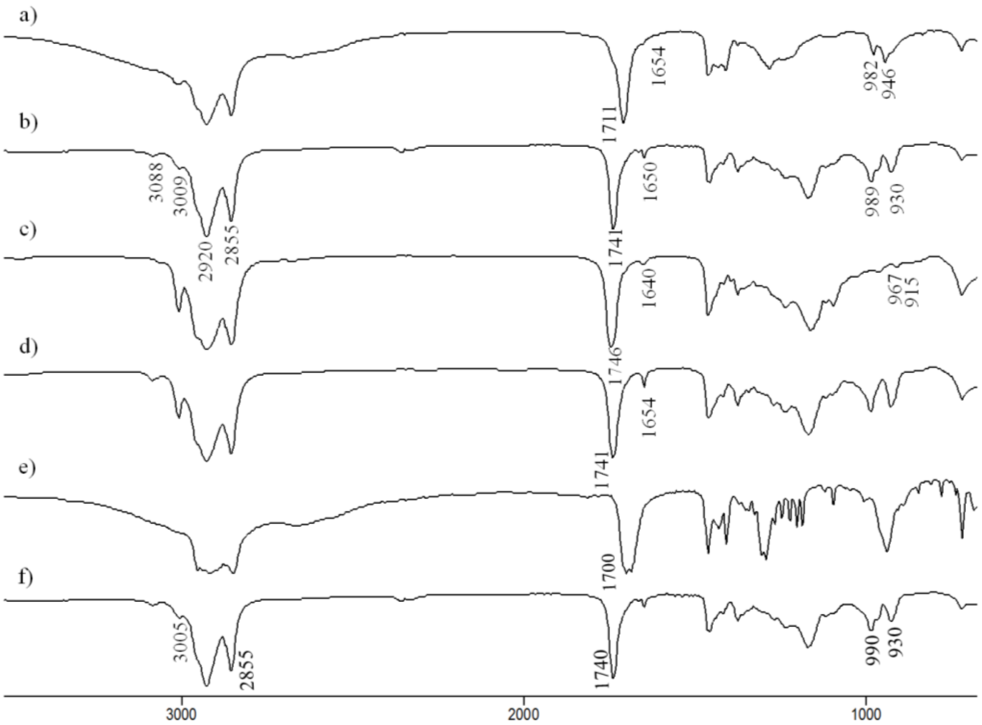

Fig. 2. 2- FTIR spectra of a) conjugated fatty acids (CFA), b) AFAD from CFA, c) soybean oil, d) AFAD from soybean oil, e) palmitic acid and f) allyl palmitate.

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 (1711 cm^{-1}), the formation of a new carbonyl band of fatty acid acyl chloride (first step) (1804 cm^{-1}) and its disappearance to be replaced by AFAD carbonyl group (second step) (1741 cm^{-1}) are shown in Fig. 2.3a. The decrease of CFA on the first 40 min and the formation of the reaction product, namely fatty acid acyl chloride are shown in Fig. 2.3b. After the disappearance of 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.

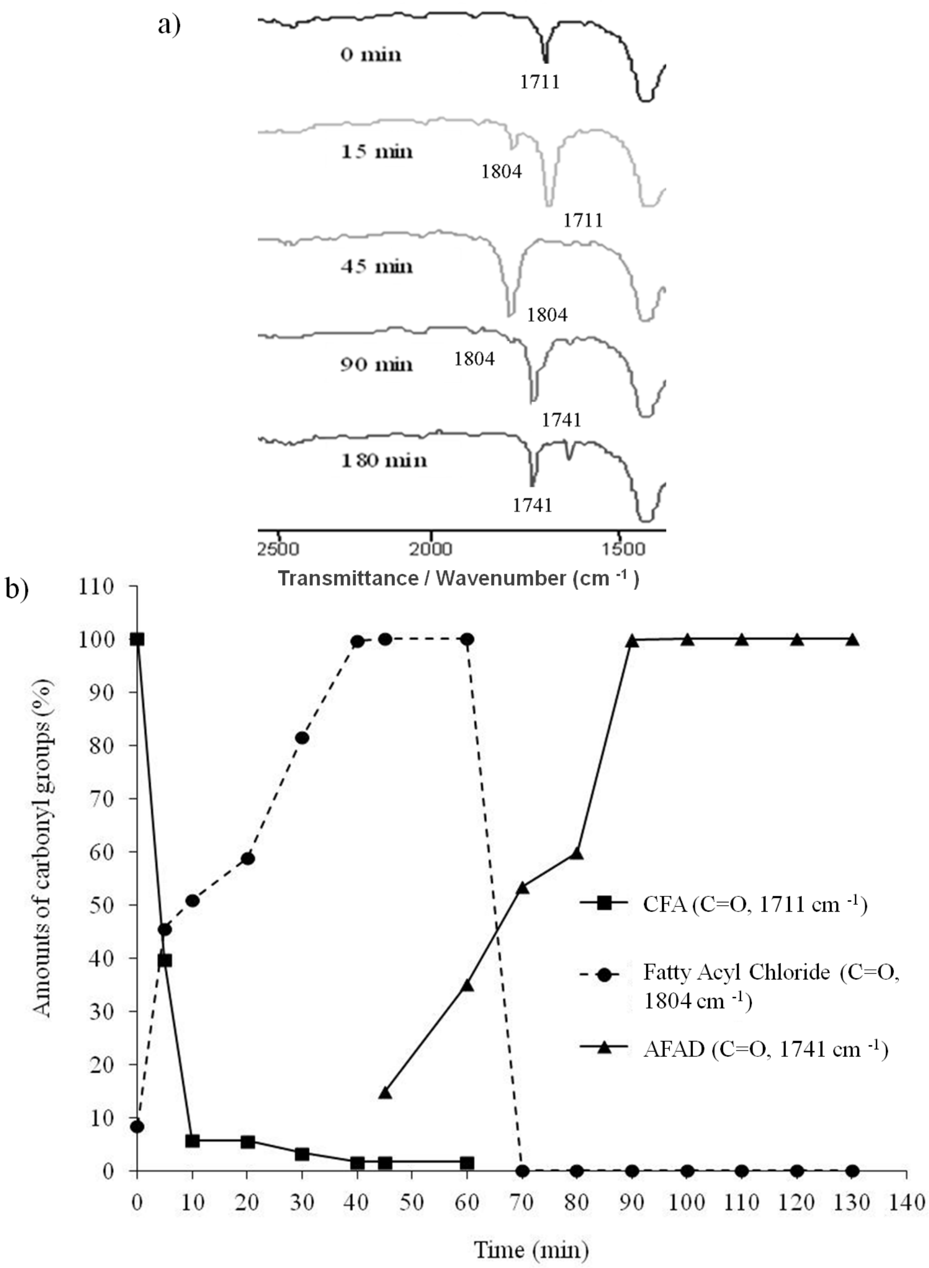

Fig. 2. 3- AFAD reactions monitored by a) infrared and b) evolution of absorptions bands during the formation of fatty acyl chloride (first step) and AFAD (second step).

2.3.2. FT-IR characterization

The characterization of the synthesized AFAD structure can be done by comparing the IR spectra of raw materials and obtained products (Fig. 2.2). All IR spectra are similar, showing the presence of two bands below 3000, namely at 2920 and 2855 cm^{-1} (saturated [$(CH_2)_n$] stretching) and one band above 3000, specifically at 3009 cm^{-1} (CH unsaturated stretching).

In all synthesis, the appearance of two bands at 930 and 989 cm^{-1}, corresponding to allylic group ((CH=CH_2, out-of-plane deformation), was observed for the reaction products. In addition, the presence of this allylic group originates the appearance at 3088 cm^{-1} of one band (unsaturated CH_2 anti symmetric stretching) and an increased intensity of bands at 1650 cm^{-1} (C=C stretching) and at 3009 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 3400 and 2400 cm^{-1}, typically from hydroxyl groups (OH stretching), and the shift of carbonyl group absorption from 1711 to 1741 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 1746 to 1741 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.

2.3.3. 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 its 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. 2.4a and 2.4b. 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 allyl group was further confirmed by GC-MS. The mass spectrum of allyl palmitate (Fig. 2.4c) was characterized by molecular ion (M) at m/z= 296, the acylium ion at m/z=239 $[M-OC_3H_5]^+$ and by a series of ions at m/z= 57, 71, 85, 113, due to the pattern fragmentation of the aliphatic chain of fatty acid of general formula $[C_nH_{2n-1}]^+$.

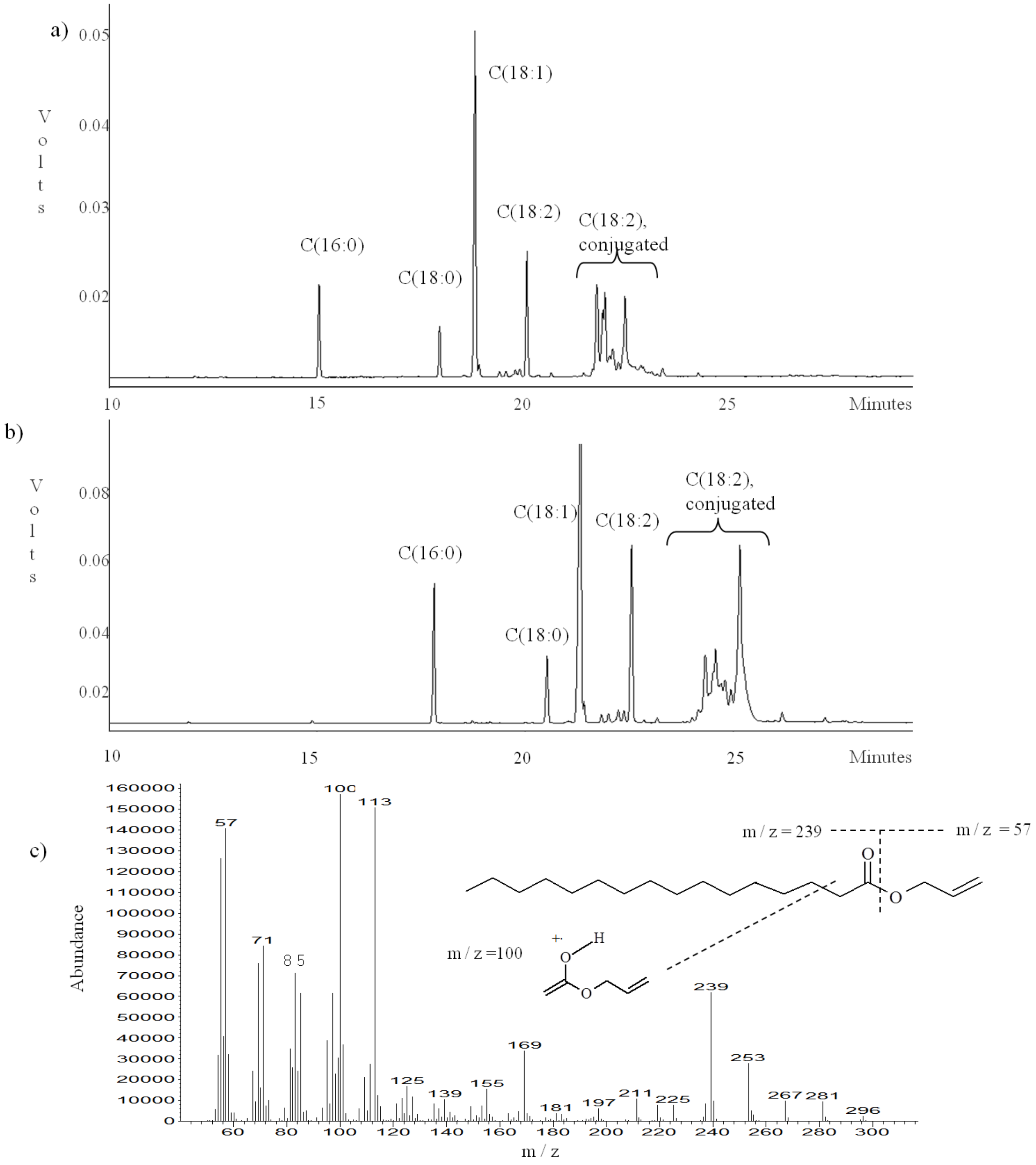

Fig. 2. 4- GC chromatogram of a) fatty acid methyl esters (FAME) from CFA, b) AFAD from CFA, c) mass spectrum of allyl palmitate.

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].

2.3.4. NMR spectroscopy

The NMR spectra of the CFA mixture, AFAD from CFA and allyl palmitate are shown in Fig. 2.5.

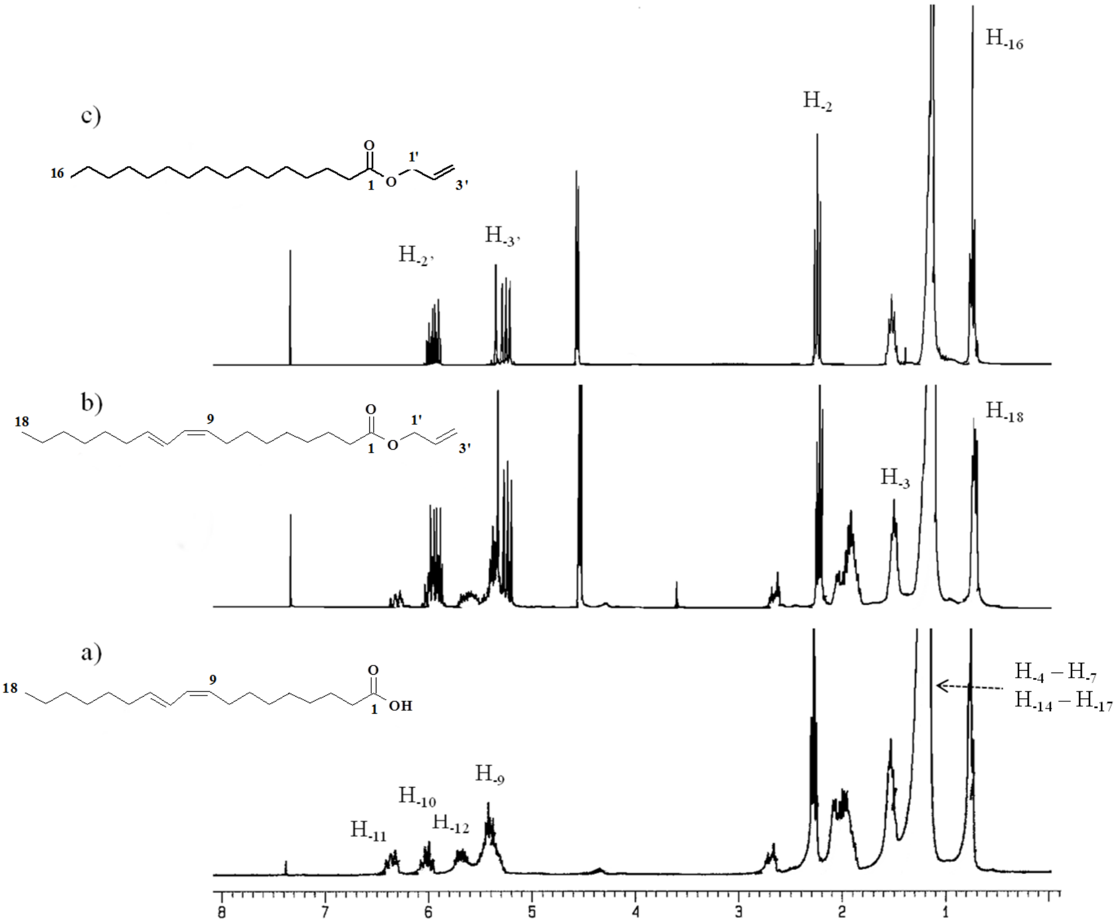

Fig. 2. 5- ^{1}H-NMR spectrum of a) conjugated fatty acid (CFA), b) AFAD from CFA, c) allyl palmitate.

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_{-18}), at δ 1.3 (*m*, aliphatic CH_2, H_{-4}-H_{-7} and H_{-14}-H_{-17}), at δ1.58 (*m*, 2H, $-C\boldsymbol{H}_2-CH_2-C(=O)-$, H_{-3}) and at δ 2.26 (*t*, 2H, $-CH_2-C(=O)-$, H_{-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 $H_{-2'}$ at δ 5.85 ppm (*ddt*, 1H, *J*= 17.2, 10.5 and 5.7 Hz, $CH_2=CH-$) and 2 $H_{-3'}$ 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. 2.5b). Additionally, the CFA spectrum (Fig. 2.5a), shows the 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 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 ^1H NMR was confirmed by ^{13}C NMR analysis (Fig. 2.6).

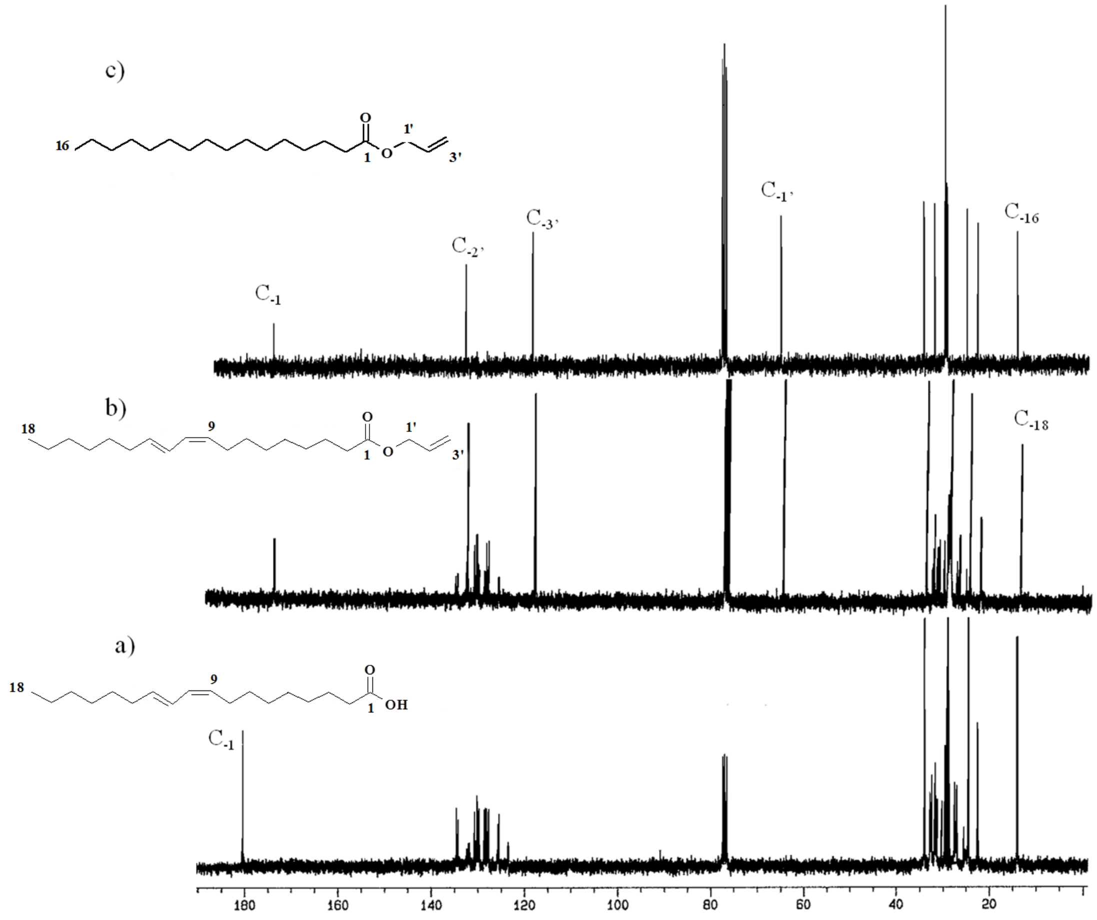

Fig. 2. 6- ^{13}C-NMR spectrum of a) conjugated fatty acid (CFA), b) AFAD from CFA, c) allyl palmitate.

The spectrum of AFAD from 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 (*C*H_2=CH-) and 132.11 ppm (CH_2=*C*H-), as the carbons of allylic group, namely

$C_{-3'}$ and $C_{-2'}$. Additionally, the characteristic signal of $C_{-1'}$ from 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].

2.3.5. Film-forming behaviour

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 wt.%, 5 wt.% 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 2.2 shows the results obtained. The addition of 5 wt.% AFAD decrease MFT significantly, from 15 ºC to 0 ºC. Higher AFAD amounts do not cause any further reduction in MFT. This shows that AFAD effectively act as a coalescing agent.

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

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

It is relevant to discuss whether AFAD can be considered a non-volatile additive in a paint formulation. Compounds are considered as volatile if the boiling point is lower than 250 ºC 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 ºC [26] and AFAD from saturated fatty acid (C18:0) has a boiling point of 401 ºC [27], it can be expected that AFAD from CFA will also have a boiling point higher than 250 ºC. Additionally, a value of 466 ºC was estimated for the boiling point of AFAD using the Joback modification of Lydersen’s group contribution method [28]. This confirms that AFAD can be considered a non-volatile component of a commercial formulation.

2.3.6. Oxidative cure behaviour

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

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 figure 2.7.

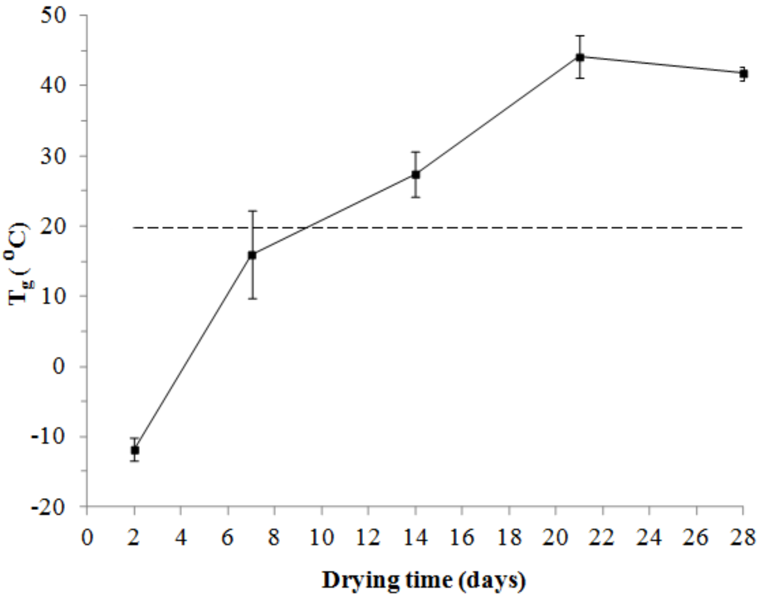

Fig. 2. 7- Glass transition temperature of mixtures of acrylic resin with 5 wt % AFAD from CFA as a function of drying time. The dashed line indicates the T_g for the pristine acrylic resin. Error bars represente standard deviations computed from 3 measurements.

The T_g of the pristine acrylic resin is also indicated, having a value of 19.6 ºC. The T_g of the dry mixture is initially -13 ºC, indicating that AFAD is 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 ºC, after 22 days. This indicates progressive hindrance of molecular mobility, due to 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 without addition of drier agents. These are a commercial catalyst combination (a mixture of cobalt, barium and zirconium) typically used for accelerating the drying rate of alkyd paints [1, 29, 30]. Table 2.3 shows the results obtained.

Table 2. 3- Drying times of physical mixtures of acrylic resin with 5 wt.% 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

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, AFAD from soybean oil (18:1) causes 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. 2.8a and 2.8b), mixtures with allyl palmitate and soybean oil have the same behaviour as the acrylic resin (less than 3 cycles to failure after 28 days), even when driers are added. The mixture with AFAD from CFA without driers shows slightly better performance (5 cycles to failure), within 7 to 14 days of drying. But when driers are added (Fig. 2.8b), the final performance is remarkably better (20 cycles to failure). The combination of AFAD from CFA with the catalyst mixture leads to an effective oxidative cure throughout the film.

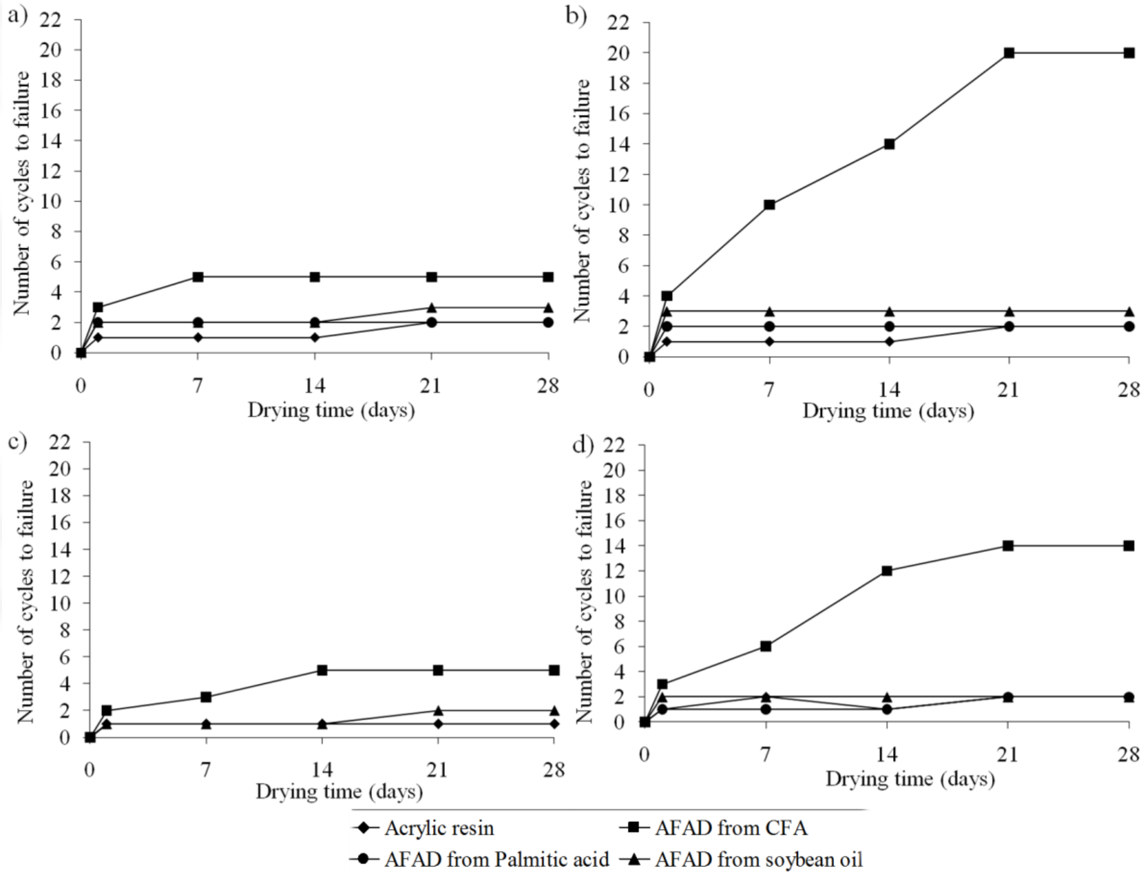

Fig. 2. 8- Rubbing resistance of acrylic resin and AFAD from CFA mixtures using two solvents a) xylene without driers, b) xylene with drier agents, c) acetone without driers, d) acetone with driers.

The rubbing resistance tests with acetone (Fig. 2.8c and 2.8d) show 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].

2.4. Conclusions

Allyl fatty acid derivative (AFAD) was 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 product 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 has a noticeable effect on the minimum film-forming temperature, decreasing it from 15 °C to 0 ºC. 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 has therefore potential interest as a non-volatile additive in waterborne coatings, acting as a coalescing agent and autoxidative crosslinking agent. This may contribute to minimize the use of volatile coalescing agents, with clear environmental and health benefits.

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Chapter 3

CHAPTER 3 - Synthesis and characterization of acrylic fatty acid derivative and use as reactive coalescing agent

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Abstract

A novel reactive coalescing agent based on vegetable oils is described. This conjugated acrylic fatty acid derivative (AcFAD) was synthesized by esterification of conjugated fatty acids (CFA) with ethylene glycol, followed by reaction with acryloyl chloride. The reactions were monitored by monitoring the acid value and by IR spectroscopy. GC–MS and NMR were used to obtain complete spectroscopic characterization of AcFAD. The potential of this conjugated derivative as reactive coalescing agent for waterborne acrylic resin formulations was evaluated in terms of drying times, minimum film-forming temperatures and solvent rubbing resistance. Significant performance improvement was observed in all tests when AcFAD was added to acrylic resin, indicating occurrence of crosslinking of conjugated double bonds upon exposure to atmospheric oxygen (i.e. oxidative cure behaviour). On the other hand, CFA addition to acrylic resin did not enhance drying behaviour or rubbing resistance of the dry films, despite the presence of conjugated double bonds as in AcFAD. This shows that introduction of (2-acryloyloxy)ethyl function plays an important role in insuring compatibility of the additive with the resin.

Keywords: Acrylic derivatives; Oxidative cure; Reactive coalescing agent; Vegetable oils; Water-borne acrylic resins

3.1. Introduction

Presently, emission of volatile organic compounds from paints and varnishes is strongly limited by environmental regulations. Thus, there is a need to develop alternatives to volatile organic compounds currently present in paints, while ensuring good film formation and drying at room temperature.

The decrease of the minimum film-forming temperature (MFT) of the polymeric binder, which is related to its glass transition temperature (T_g), through the appropriate choice of monomer composition may exempt the use of solvents (coalescing agents) in the paint. However, this approach often leads to tacky films after drying.

One alternative is the use of special comonomers [1–3] or non-volatile additives [4, 5] capable of decreasing the MFT. During film drying, in parallel with polymer particle coalescence, oxidative curing of the existing unsaturated double bonds takes place, forming a hardened, non-tacky, crosslinked structure [6–9]. The type of double bonds (conjugated or non-conjugated) has a significant effect on the reaction mechanism [10]. Non-conjugated double bonds lead to radical recombination in the form of dimers [11–13]. With conjugated fatty acids (CFA), more effective crosslinking occurs, due to a chain addition mechanism [8, 14].

In the present study, a conjugated acrylic fatty acid derivative (AcFAD), obtained from vegetable oils, was synthesized considering a two-step reaction consisting of a CFA esterification with ethylene glycol (EG) at high temperatures and followed by the fatty acid glycol ester (FAGE) reaction with acryloyl chloride (AC). It must be noted that alternative synthesis routes can be followed, like direct condensation of 2-hydroxyethyl acrylate with CFA or the corresponding methyl ester derivatives [15]. The synthesized novel product was chemically characterized, and its performance as a reactive coalescing agent in combination with a commercial acrylic resin was evaluated.

3.2. Experimental

3.2.1. Materials

Sunflower oil conjugated fatty acids (CFA), ethylene glycol (EG), xylene and dibutyltin oxide and a commercial acrylic polymer emulsion (product specification states that free residual monomer is less than 300 ppm) were kindly supplied by Resiquímica - Resinas Químicas, S.A. (Mem Martins, Portugal).

Acryloyl chloride (AC) and dichloromethane were purchased from Fluka; petroleum benzin, ethanol, diethyl ether and phenolphthalein from Merck; potassium hydroxide (KOH), anhydrous magnesium sulphate ($MgSO_4$) and anhydrous calcium chloride ($CaCl_2$) from Panreac; deuterated chloroform ($CDCl_3$, 99.8 % D) from Sigma-Aldrich. All chemicals were used as received. Triethylamine and drying catalyst (3 % cobalt, 3 % barium and 5 % zirconium) were kindly dispensed by CIN – Corporação Industrial do Norte (Maia, Portugal).

3.2.2. Characterization methods

Acid value was determined by volumetric titration. The sample was added to a titrand solution (a mixture of xylene, ethanol and phenolphthalein indicator) and neutralized with 0.1M KOH aqueous solution until the appearance of the first permanent pink colour.

Infrared (IR) spectra were recorded with an ABB - Bomen spectrometer, the liquid samples being placed in a sodium chloride cell. Each spectrum was an average of 32 scans taken with 4 cm^{-1} resolution in the 4000-650 cm^{-1} range.

NMR spectra were recorded on a Bruker Avance III - 400 spectrometer operating at a frequency of 400 and 100 MHz, respectively ^1H NMR and ^{13}C NMR. The samples were dissolved in deuterated chloroform ($CDCl_3$). Chemical shifts were reported in part per million (ppm, δ) and referenced to $CDCl_3$. ^1H-NMR, ^{13}C-NMR, APT, HSQC and HMBC correlation techniques were applied to assign the chemical shifts of proton and carbon atoms.

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 5973N - Agilent with electron impact ionization chamber. GC separation was performed on DB-5MS J&W capillary column (30 m x 0.25 mm I.D., 0.25 μm film thickness). Helium was used as carrier gas with a constant flow of 1 ml min^{-1}. The injection was made in split mode (40:1) at 250 ºC. 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 ºC at 3 ºC min^{-1} for 13 min. The MS transfer line temperature was held at 280 °C. Mass spectrometric parameters were set as follows: electron impact ionization with 70 eV energy; ion source temperature, 230 ºC and MS quadrupole temperature, 150 ºC. The MS system was routinely set in full scan mode. Agilent Chemstation was used for data collection/processing and GC-MS control.

Mixtures of 5 wt.% AcFAD or CFA with acrylic resin were prepared by mixing the resin under vigorous stirring for 30 min. Films were then obtained by doctor-blading on a glass surface and drying at room conditions. In some cases, oxidative cure driers—a commercial catalyst combination of cobalt, barium and zirconium, typically used for accelerating the drying rate of alkyd paints—were added to the mixtures.

Drying times were then determined by applying 100 μm wet thickness films on 10 cm x 15 cm glass plates of size and measuring the time until the surface was dry to the touch. The drying times presented are an average for at least three films.

Minimum film forming temperature was determined according to standard procedure ISO 2115:1996—plastics– polymer dispersions—determination of white point temperature and MFT.

The solvent resistance of the films was determined by performing a rubbing test. Rubbing was performed manually with a cotton piece previously wet in xylene or propanone, along a 5 cm length of the dried film. The values reported are the number of cycles (double rubs) until film failure and representan average of the results obtained for at least two films.

3.2.3. AcFAD synthesis

Conjugated fatty acids were charged into a three-necked round bottom flask (150 g, 0.54 mol), equipped with magnetic stirrer, thermometer, nitrogen purge and water condenser. Reaction occurred at 200 ºC in the presence of dibutyltin oxide (0.02 wt.%, based on the amount of CFA). EG (33 g, 0.54 mol) was added dropwise for 2 h. Samples were withdrawn at intervals of 1 h and the acid value determined. The reaction was continued until the acid value be below 10 mg KOH/g. The reaction product was placed in a separating funnel overnight, in order to separate the excess EG. The organic phase was mixed with diethyl ether, washed with 10 portions of 100 mL of distilled water and dried overnight with anhydrous magnesium sulphate. Finally, solvent was removed under vacuum and the FAGE obtained (yield 92%).

The FAGE previously synthesized (100 g, 0.39 mol) was mixed with dichloromethane (432 g, 4.86 mol) and triethylamine (50 g, 0.49 mol) at room temperature and placed into a threenecked round bottom flask equipped with magnetic stirrer, thermometer, nitrogen purge and water condenser. AC (30 g, 0.33 mol) was mixed with dichloromethane (164 g, 1.84 mol) and added dropwise for 2 h. The reaction was continued for 3 h to maximize production of AcFAD. The reaction was monitored via IR spectroscopy.

The reaction mixture was purified by liquid extraction in a separating funnel, and washed with petroleum benzin and distilled water, until neutralization. The organic layer was dried overnight with anhydrous calcium chloride and filtered. Finally, the solvent was removed under vacuum and the product obtained (yield 86%) was characterized by fourier transformed infrared (FT-IR), NMR and GC–MS.

3.3. Results and discussion

To the best of our knowledge, the synthesis of AcFAD, an (2-acryloyloxy)ethyl derivative of the complex mixture of CFA, has not been reported before. Its complete characterization is therefore presented next.

3.3.1. Synthesis and AcFAD characterization by FT-IR

AcFAD was synthesized by conjugated fatty acids (CFA) esterification (first step) with ethylene glycol (EG) followed by esterification with acryloyl chloride (AC, second step). The overall reaction is presented in Fig. 3.1.

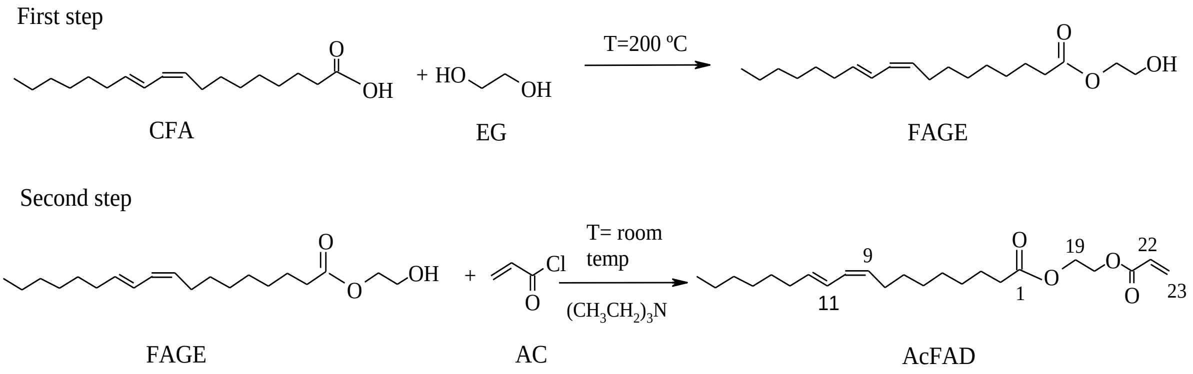

Fig. 3. 1– Reactions involved in AcFAD synthesis process.

Fatty acid glycol ester (FAGE) synthesis (first step) was followed by the decrease in the acid value of the reaction product. As shown in Fig. 3.2-i), in the first hour there is a significant decrease in the acid value from 207 to 54 mg KOH/g, followed by a slow decrease along 5 hours. The esterification reaction was stopped when the acid value was close to zero (7 hours of reaction).

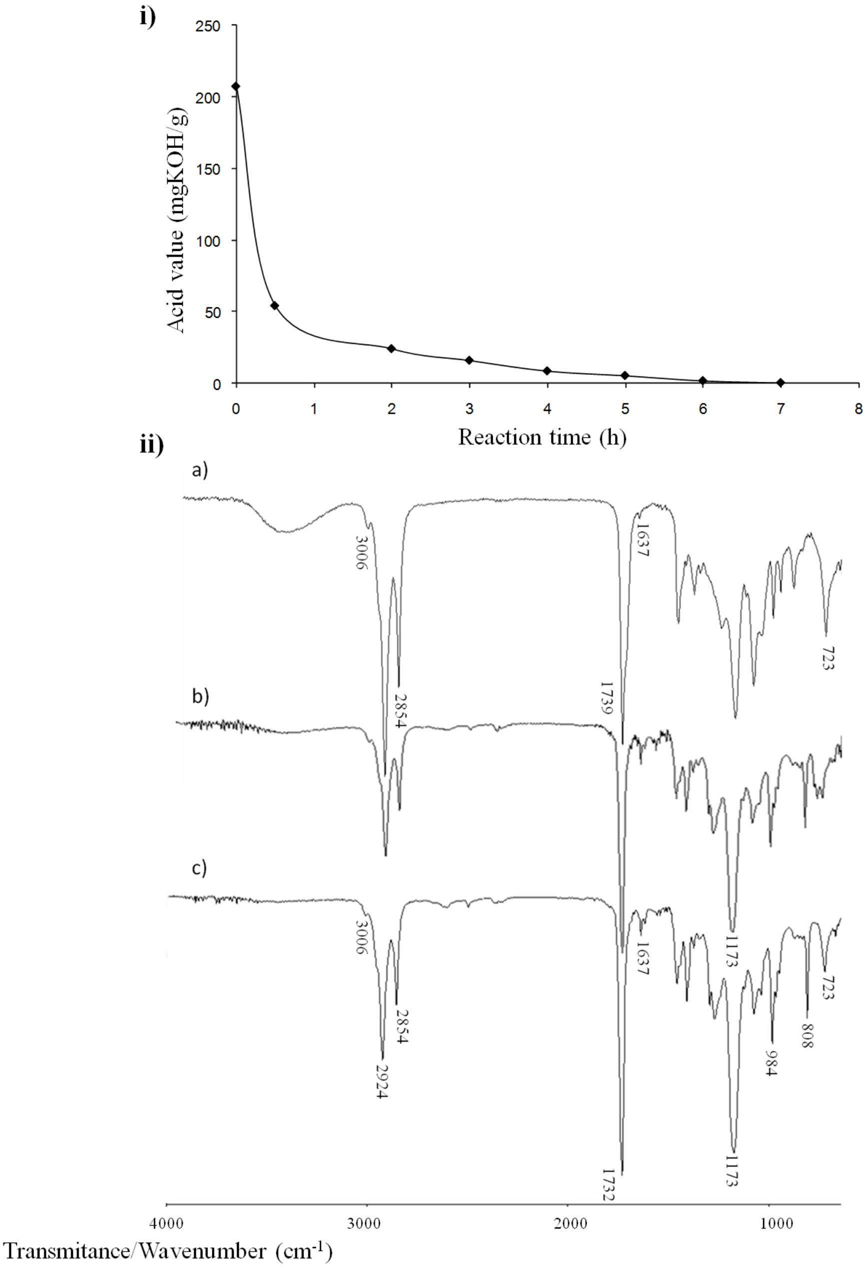

Fig. 3. 2- Monitoring acid value of the reaction product during the esterification reaction (first step) (i) and FAGE reaction (second step) by IR ii): (a) t = 0 h (FAGE); (b) t = 1 h and (c) t = 2 h.

The effect of the CFA:EG molar ratio on the esterification equilibrium conversion was studied. The proportion of fatty acid glycol ester (FAGE) and fatty acid glycol diester (FAGDE) in the reaction product was determined by ^{1}H NMR analyses. The ratio of the signal areas was determined at δ 4.2 and δ 3.6 ppm (Fig. 3.3), which are respectively assigned to $RCOO\text{-}CH_2\text{-}C\underline{\mathbf{H}}_2\text{-}OCOR$ from FAGDE and $RCOO\text{-}CH_2\text{-}C\underline{\mathbf{H}}_2\text{-}OH$ from FAGE.

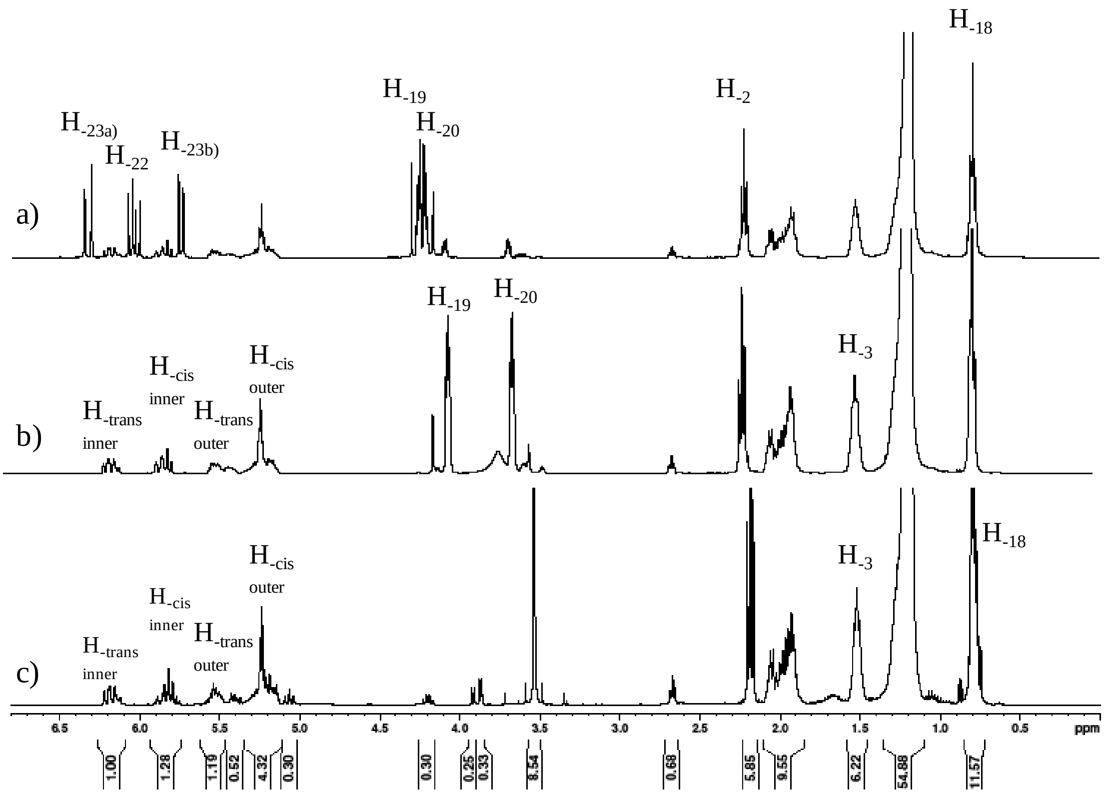

Fig. 3. 3- ^{1}H NMR spectra of (a) AcFAD, (b) FAGE and (c) FAME.

Table 3.1 shows the results for different CFA:EG molar ratios. The conversion into FAGE was very satisfactory (92 %) with a CFA:EG (1:15) molar ratio. Thus, this ratio was assumed for the FAGE synthesis in the ensuing work.

Table 3. 1- Molar ratio and conversions percentages of the CFA esterification reaction products, determined by ^{1}H NMR analyses.

CFA:EG	% FAGE	% FAGDE
1:3	60	40
1:6	85	15
1:16	92	8

The second reaction step was followed by IR-spectroscopy. Fig. 3.2-ii) shows the results: 1) disappearance of the OH stretching (3400-3200 cm^{-1}) band, characteristic of hydroxyl group and presents in FAGE; 2) small shift of carbonyl group band of fatty acid glycol ester from 1739 to 1732 cm^{-1}; 3) increase of intensity in the peak at 1637

cm^{-1} (C=C, stretching), due to the incorporation of the acrylic double bond. These results confirm the occurrence of AcFAD synthesis.

Additionally, the AcFAD structure was characterized by IR spectra. Fig. 3.2-ii,c) shows the band at 3006 cm^{-1} (CH, unsaturated stretching) corresponding to the double bonds of the aliphatic chain and two bands at 2924 and 2854 cm^{-1} (saturated $[(CH_2)_n]$, stretching). The appearance of only one absorption band relative to the carbonyl group at 1732 cm^{-1}, is a consequence of the overlapping of two distinct carbonyl groups (C=O stretching) at 1739 cm^{-1} (from a saturated carbonyl ester as in FAGE) and a 1726 cm^{-1} (from an additional unsaturated carbonyl ester) [16]. On the other hand, an increased intensity of bands at 1173 cm^{-1} (C-O, stretching) in AcFAD spectrum was also observed due to the introduction of other ester group.

Moreover, the emergence of two bands at 984 and 808 cm^{-1} ($CH=CH_2$, out-of-plane deformation) are assigned to terminal acrylic double bonds, as the band at 723 cm^{-1} ($CH=CH_2$, out-of-plane deformation) which is overlapped by the $[(CH_2)_n]$ rocking vibration, relative to the aliphatic chain.

3.3.2. GC–MS characterization

The conjugated fatty acids (CFA) used in this study were a complex mixture used as an industrial raw material, which composition was analyzed by GC-FID of its fatty acid methyl esters [16]. The main components of CFA are C18 fatty acids with one double bond (27 %) and two conjugated bonds (48 %) frequently assign as Conjugated Linoleic Acid (CLA). The four most abundant CLA isomers have double bond geometry E/Z or Z/E: 9Z, 11E; 10E, 12Z; 8E, 10Z and 11Z, 13E [8, 17, 18]. Additionally, the C18 fatty acids with two non-conjugated double bonds (11 %) and C16 saturated (7 %), are also represented in the mixture.

The chromatographic profiles of the methyl and the acrylic derivatives in GC-MS are similar, only with a delay in the retention time (16-18 min), due to the substitution of a methyl group by a glycolacrylate function.

The functionalization of CFA by the acrylic group was confirmed by GC-MS in all the peaks of the chromatogram. The AcFAD mass spectra are characterized by intense ion fragments at *m/z*= 55 and 99, characteristic of the acryloyl ion $[CH_2{=}CH\text{-}CO]^+$ and the glycol acrylated ion $[CH_2{=}CH\text{-}COO\text{-}CH_2CH_2]^+$, respectively [19]. The high intensity of these peaks is due to the extended electron *π*-system, which leads to the most stable ions observed in the fragmentation of these compounds.

Additionally, ion *m/z*=M-116 was observed in all the mass spectra, due to the elimination of a neutral molecule, $CH_2{=}CH\text{-}COO\text{-}CH_2CH_2OH$ (characteristic of the ethylene glycolacrylates) [20] allowing the detection of the molecular ion, $[M]^+$, and the identification of each chromatographic peak.

3.3.3. Characterization of AcFAD by NMR spectroscopy

The AcFAD structure was also confirmed by NMR spectra. The assigned data were based on COSY, HSQC and HMBC techniques. Since C18 fatty acids correspond to 86 % in total content of CFA mixture, AcFAD structure was represented using the 9Z, 11E of C18:2 (rumenic acid). The ^{1}H NMR spectra analysis (Fig. 3.3) shows the typical resonances of the saturated aliphatic chain ($[(CH_2)_n]$ between δ 3 and 0 ppm, namely at δ 2.24 (*t*, *J*= 7.2 Hz, $\text{-}C\underline{\mathbf{H}}_{\mathbf{2}}\text{-}C(=O)\text{-}$, $H_{\text{-}2}$), at δ 1.52 (*m*, 2H, $\text{-}C\underline{\mathbf{H}}_2\text{-}CH_2\text{-}C(=O)\text{-}$, $H_{\text{-}3}$), at δ 1.19 (*m*, aliphatic $C\underline{\mathbf{H}}_{\mathbf{2}}$, $H_{\text{-}4}$-$H_{\text{-}7}$ and $H_{\text{-}12}$-$H_{\text{-}17}$) and at δ 0.79 (*t*, *J*= 7.2 Hz, $C\underline{\mathbf{H}}_3$, $H_{\text{-}18}$).

The region between δ 6.5 and 5 ppm is relative to the aliphatic and acrylic double bonds and was compared to the same region of the methyl derivatives (FAME), which allows differentiating the peaks referent to FAGE and AcFAD (Fig. 3.3). According to Davis and co-workers [21], the 4H from the conjugated double bonds ($C\underline{\mathbf{H}}{=}C\underline{\mathbf{H}}\text{-}C\underline{\mathbf{H}}{=}C\underline{\mathbf{H}}$, C18:2) of the main CLA's isomers (9Z, 11E and 10E, 12Z), appear at δ 6.24 (H-*trans* inner, *dd*, *J*=15.0 and 11.0 Hz), 5.80 (H-*cis* inner, *t*, *J*=11.0 Hz), 5.51 (H-*trans* outer, *dt*, *J*=15.0 and 7.0 Hz), and 5.38 ppm (H-*cis* outer, *dt*, *J*=11.0 and 7.0 Hz). These were also in accordance with the data obtained individually for each CLA isomer [22]. Additionally, the 4H from non-conjugated double bonds ($C\underline{\mathbf{H}}{=}C\underline{\mathbf{H}}\text{-}CH_2\text{-}C\underline{\mathbf{H}}{=}C\underline{\mathbf{H}}$, C18:2) of the CFA mixture and the 2H from oleic acid double bond (C18:1 Δ^{9Z}) were all overlapped between δ 5.3-5.1 ppm. Three acrylic ester protons appear at δ 6.33 ppm (*dd*, 1H, *J*=17.4 and 1.2 Hz, $\mathbf{C}\underline{\mathbf{H}}_{\mathbf{2}}{=}CH\text{-}$, $H_{\text{-}23b}$), δ 6.04 ppm (*dd*, 1H, *J*= 17.4 and 10.4 Hz, $CH_2{=}\mathbf{C}\underline{\mathbf{H}}\text{-}$, $H_{\text{-}22}$) and at δ 5.76 ppm (*dd*, 1H, *J*=10.4 and 1.2 Hz, $\mathbf{C}\underline{\mathbf{H}}_{\mathbf{2}}{=}CH\text{-}$, $H_{\text{-}23a}$).

The peak integration ratio between δ 2.7 (CH_2 doubly allylic) and 2.2 ppm (CH_2CO) allows to determine the percentage of the two non-conjugated double bonds in the C18 fatty acids (11 %), which is according to the data previously obtained from the GC-FID.

The AcFAD ^{13}C NMR and APT (Attached Proton Test) extension spectra were compared. Two peaks were identified as the carbonyl ester carbons at δ 173.3 and 165.6 ppm (C=O, respectively saturated, C_{-1}, and unsaturated, C_{-21}). The region between δ 135 and 125 ppm shows several ethylenic carbons evidencing two peaks with higher intensity at δ 131.0 ppm ($\underline{\mathbf{C}}H_2$=CH-) and 127.9 ($CH_2$=$\underline{\mathbf{C}}$H-), corresponding to acrylic carbons, specifically C_{-23} and C_{-22}. The other signals in this region come from the different conjugated fatty acids present in the CFA mixture. Thus, the signals assigned to the 4 isomers E,Z/Z,E (9Z, 11E; 10E, 12Z; 8E, 10Z and 11Z, 13E) are easily identified, due to the appearance of 4 groups of 4 signals (Fig. 3.4) around δ 133.6 (CH-*trans* outer), δ 129.5 (CH-*cis* outer), δ 128.4 (CH-*cis* inner), δ 125.4 ppm (CH-*trans* inner), which are assigned to the isomers 9Z, 11E; 10E, 12Z; 8E, 10Z and 11Z, 13E [18, 19] and represent the main components of CLA mixture [23].

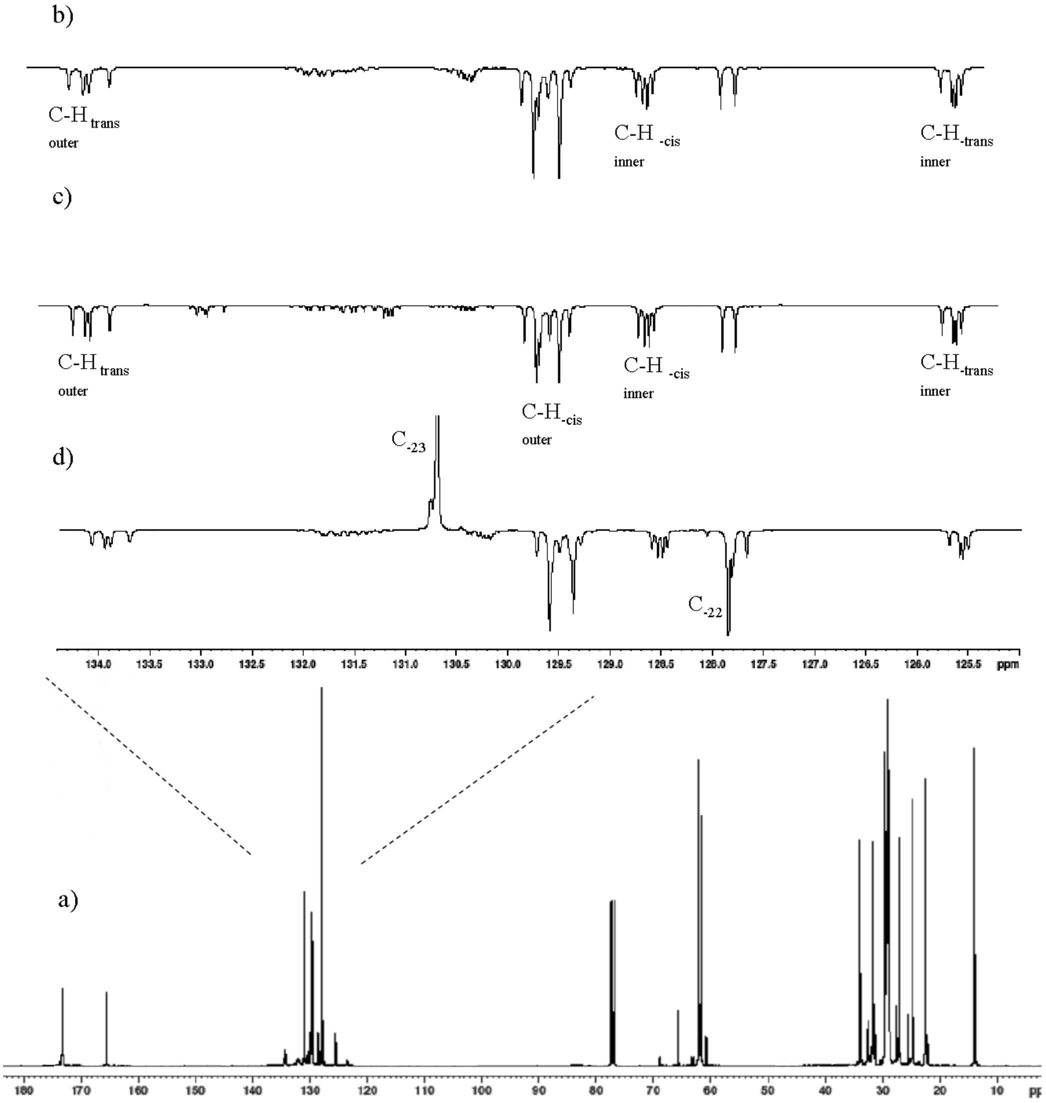

Fig. 3. 4- ^{13}C NMR spectrum of (a) AcFAD and attached proton test extension spectra between d 125 and 134 ppm of (b) FAGE, (c) FAME and (d) AcFAD.

All the peak assignments were confirmed by ^{1}H-^{13}C HSQC technique (Heteronuclear Single Quantum Correlation) (Fig. 3.5). This technique is very useful to identify complex molecules spectra as AcFAD, since it allows the correlation between the proton chemical shift value and the ^{13}C directly attached to it. So, the most complex regions of AcFAD in NMR spectra, corresponding to aliphatic chain (between δ 34 and 22 ppm, $[(CH_2)_n]$) and double bonds (between δ 135 and 125 ppm), could be easily assigned by observing correlations between ^{1}H and ^{13}C nucleus. These are according to the mixture of geometric fatty acid isomers with different stereochemistry and unsaturation levels [21, 23]. The signals at δ 6.24, 5.80 and 5.51 ppm are directly linked to the carbons at δ 125.4 (CH-*trans* inner), 128.4 (CH-*cis* inner) and 133.6 ppm (CH-*trans* outer), respectively, while the correlation between the carbons at δ 130-129 (CH-*cis* outer) and δ 5.38 ppm, allow to clearly identify the *cis*-outer olefin proton, which is overlapped by the olefins protons from oleic and linoleic derivatives (Fig. 3.5a). On the other hand, the signal of C_{-22} acrylic carbon, at δ 127.9 ppm (CH) was directly linked to the proton at δ 6.04, while the C_{-23} at δ 131.0 ppm (CH_2) were attached to the protons at δ 5.76 and 6.33 ppm.

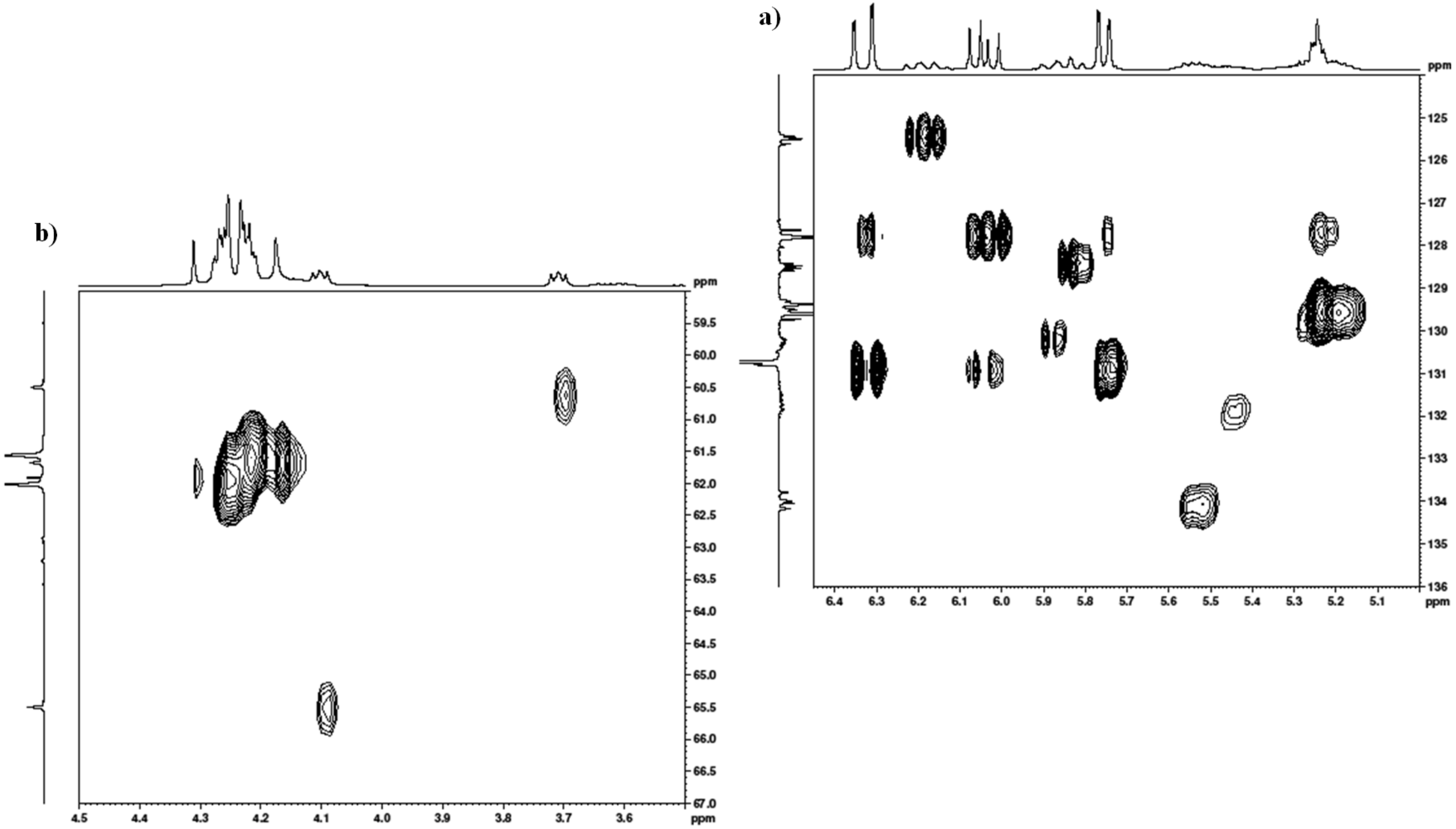

Fig. 3. 5 - Acrylic fatty acid derivative (AcFAD) ^{1}H-C^{13} HSQC spectrum: a) region assigned to acrylic and conjugated aliphatic double bonds and b) region between δ 3.5 and 4.5 ppm.

Additionally, the assignments of the two triplets at δ 4.27 (2H, *J*= 7.2 Hz, H-$_{20}$) and δ 4.22 ppm (2H, *J*=7.2 Hz, H-$_{19}$) characteristic of hydrogens directly attached to the oxygen atom (–O-C**H**$_2$, H$_{-19}$ and H$_{-20}$), were made based on the expected chemical shifts. These values were also confirmed by Heteronuclear Multiple Bond Correlation (HMBC) technique (Fig. 3.6), which is used to correlate the chemical shift value between the proton and a carbon two or three bonds away. Thus, HMBC allows to confirm that the H$_{-19}$ (δ 4.22 ppm) where correlated with the saturated carbonyl group (δ 173.3 ppm, C$_{-1}$), while the H$_{-20}$ (δ 4.27 ppm) were correlated to the unsaturated carbonyl group (δ 165.6 ppm, C$_{-21}$). On the other hand, HSQC spectrum (Fig. 3.5b) confirmed that the signals at δ 4.27 and 4.22 ppm, where directly linked to δ 62.1 and δ 61.7 ppm (-CO-O-**C**H$_2$-**C**H$_2$-O-CO-), respectively C$_{-20}$ and C$_{-19}$.

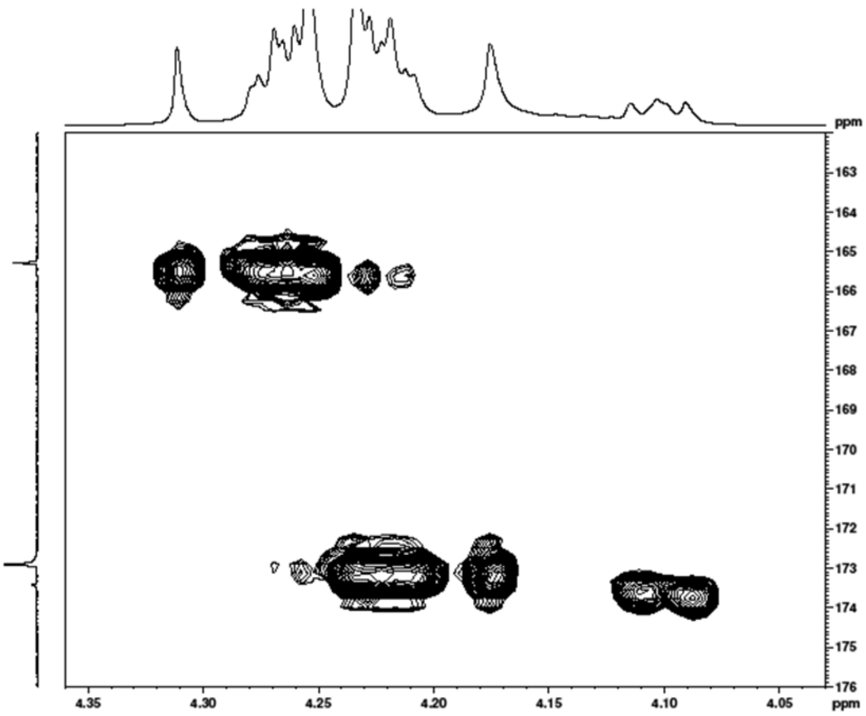

Fig. 3. 6 - Acrylic fatty acid derivative (AcFAD) ^{1}H-C^{13} HMBC spectrum.

3.3.4. Film forming and oxidative cure performance

Table 3.2 shows the drying times for AcFAD and CFA, mixed with driers. As expected, both products have autoxidative drying properties, due to the presence of conjugated double bonds. However, AcFAD shows faster drying than CFA, due to the presence of hydroxyethyl acrylate group with a very reactive C— C conjugated double bond.

Table 3. 2- Drying times of AcFAD and CFA mixed with driers.

	t [h]
AcFAD	24 h - 48 h
CFA	48 h – 74 h

This is a pertinent result, since if CFA displayed an equally efficient oxidative cure performance then synthesis of an acrylic derivative would not be relevant. Table 3.3 completes the comparison between AcFAD and CFA, now in terms of coalescing agent performance when combined with acrylic resin. Addition of AcFAD significantly decreases drying time and MFT. CFA, on the other hand, do not introduce substantial changes.

Table 3. 3- Drying times, MFT and film appearance of physical mixtures of acrylic resin with 5 wt.% of AcFAD and CFA, mixed with driers.

Mixtures	**Drying time [min]**	**MFT [º C]**	**Film appearance [1 - poor, 5 – good]**
Resin	54	15	4
Resin + AcFAD	39	-2	4
Resin + CFA	53	5	2

Most importantly, the appearance of the films formed is very different in the two cases. The mixture of CFA with resin yields a heterogeneous looking surface, with small blisters, indicating incompatibility between CFA and resin. The carboxylic groups in CFA will be partially deprotonated at the resins slightly basic pH, forming highly hydrophilic carboxylate anions. This probably leads to micellization in the aqueous medium, in detriment of adsorption on the already anionically stabilized polymer emulsion. After water evaporation, phase segregation occurs between CFA and the coalescing polymeric film, originating surface irregularities. AcFAD, on the other hand, contains a non-ionic hydroxyethyl acrylate group, which probably promotes adsorption at the polymer particles surface, and interpenetration upon film drying.

A rubbing resistance test was made to evaluate the occurrence of oxidative cure during the drying of mixtures of acrylic resin with AcFAD and CFA. The drying films were exposed to air for 6 week. Two solvents with different polarities - xylene and propanone - were used in the rubbing tests.

For rubbing test with xylene (Fig. 3.7a), mixtures incorporating AcFAD show superior performance than the acrylic resin (eight more cycles to failure after 5 week), this behavior being more evident when driers are added (24 more cycles to failure after 5 week). Similar behaviour is obtained for the rubbing resistance test with propanone (Fig. 3.7b). However, the performances are not as good, since the acrylic resin has a higher affinity for a polar solvent like propanone, weakening the rubbing resistance. In both cases, rubbing resistance increases along drying time, demonstrating the progressive oxidative cure of the AcFAD chains. The relatively slow rate of this curing process is expectable for this type of system [8]. Results for mixtures of resin with CFA, with or without driers (not shown), did not display any improvement in relation to the resin alone.

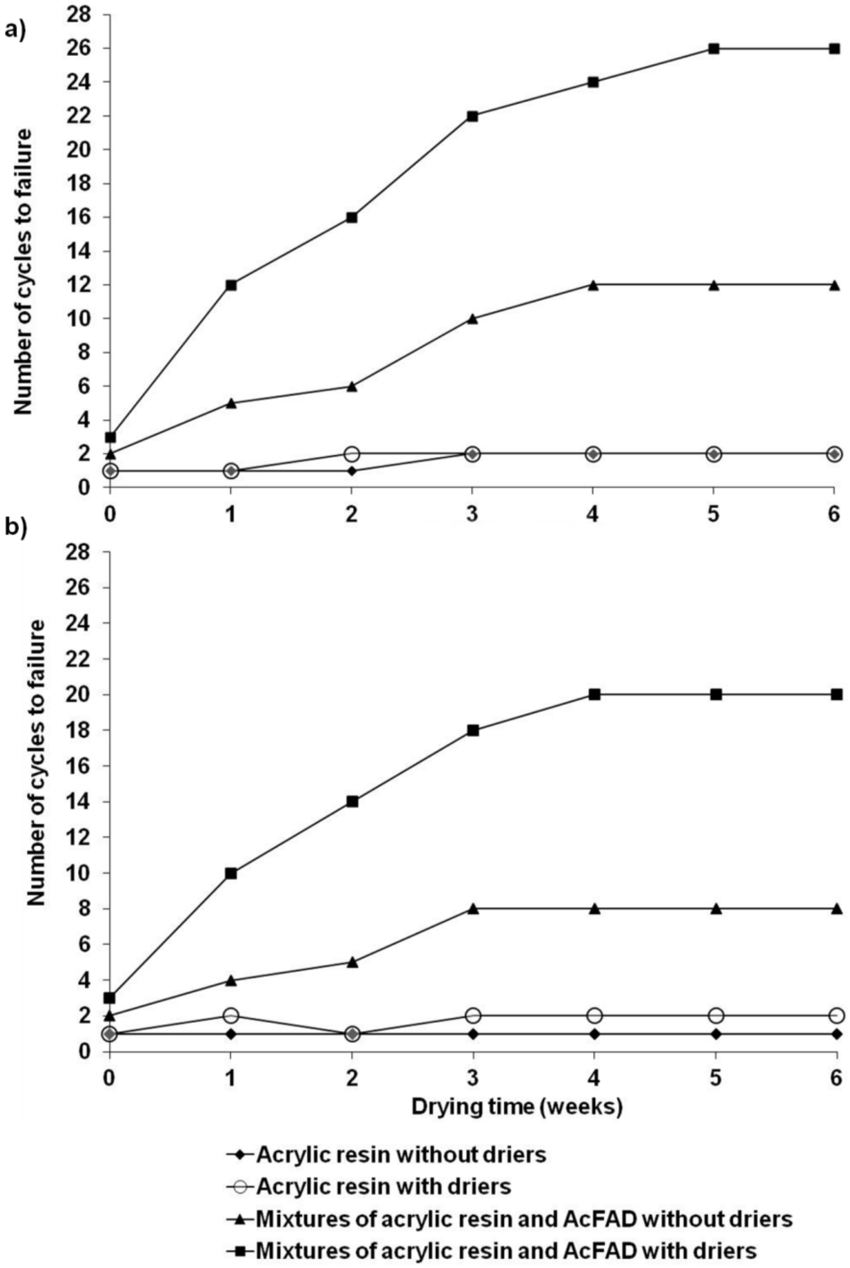

Fig. 3. 7– Rubbing resistance of acrylic resin and AcFAD mixtures with or without driers, using xylene (a) and propanone (b).

The reaction between the conjugated double bonds in AcFAD and atmospheric oxygen, during drying, leads to the progressive formation of crosslinked structures, increasing rubbing resistance and decreasing drying times and MFT. AcFAD therefore effectively acts as a reactive coalescing agent.

3.4. Conclusions

Acrylic fatty acid derivative was synthesized by CFA esterification with EG followed by esterification with AC. The two reactions involved were monitored by determination of acid value and FT-IR spectroscopy, respectively. FT-IR and NMR were used to identify the chemical structure of the AcFAD produced. The introduction of HSQC and HMBC techniques allowed a better assignment in the correlations between hydrogens and carbons, namely in the region of the acrylic and conjugated double bonds.

Addition of 5 wt.% AcFAD to commercial acrylic resin decreased substantially the drying time and MFT, while maintaining good film appearance. Rubbing resistance tests indicated that AcFAD addition also improves solvent resistance.

The incorporation of AcFAD, obtained from renewable resources, in waterborne acrylic resins provides auto-oxidative crosslinking, allowing film formation and intrinsic film hardening without the need of volatile organic co-solvents.

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Chapter 4

CHAPTER 4 - Incorporation of an acrylic fatty acid derivative as comonomer for oxidative cure in an acrylic emulsion

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Abstract

An acrylic fatty acid derivative (AcFAD) was prepared by solvent homo- and co-polymerization and by emulsion copolymerization, and the final products characterized. In solvent polymerizations, NMR analyses confirmed that the reaction occurs both by the terminal acrylic double bond and by the conjugated doubles bonds present in the aliphatic chain. In emulsion polymerization, the emulsion formulation and reaction procedure was optimized in order to allow incorporation of AcFAD in a commercial acrylic resin formulation. Polymerization reaction involving both types of double bonds was again confirmed by NMR analyses.

Compared with the reference acrylic resin, the results obtained after AcFAD incorporation showed time-dependent increase in gel content and in rubbing resistance. These were ascribed to oxidative cure and consequent self-crosslinking of the acrylic polymer, involving the conjugated double bonds in the AcFAD side-chains. The oxidative cure was also confirmed by FT-IR analyses. Reduction in minimum film-forming temperature (MFT) also evidenced that AcFAD has an internal plasticization effect during film formation. Incorporation of this comonomer in acrylic paint binder formulations constitutes a promising alternative to the use of volatile coalescing agents.

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

4.1. Introduction

Environmental regulations are been imposing increasingly more limitations to the emission of volatile organic compounds (VOC) to atmosphere, since this leads ultimately to the formation 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 development of polymeric binders for paint formulations that allow film formation at room temperature without the need for volatile coalescing agent addition. 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 [3-4]. Incorporation of fatty acid derivatives, derived from renewable resources, as comonomers in emulsion polymers has been suggested [5, 8] as a strategy for obtaining waterborne paint binders capable of oxidative cure. These do not depend on coalescing agent evaporation for obtaining a hard, non-tacky, dry film. Additionally, the drying rates can be accelerated by addition of catalytic driers [9-11].

In this study, two different approaches to free radical addition polymerization [12] 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 [13, 14]. The resulting products from acrylic fatty acid derivatives (AcFAD) homo and copolymerization were characterized, focusing on its potential use.

4.2. Experimental

4.2.1. Materials

A mixture of conjugated fatty acids (CFA) derived from sunflower oil, a commercial acrylic polymer emulsion (product specification states that free residual monomer is less than 300 ppm), xylene, benzoyl peroxide (BP), methyl methacrylate (MMA), butyl acrylated (BA), acrylic acid (AA), (Hydroxyethyl)methacrylate (HEMA), dodecyl benzene sulfonic acid sodium salt (DBSA), fatty alcohol ether sulfosuccinate disodium salt (FAES), ethoxylated alkyl sulphate, sodium persulfate, dibutyltin oxide were kindly supplied by Resiquímica - Resinas Quimicas, S.A. (Mem Martins, Portugal).

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 – Corporacão Industrial do Norte (Maia, Portugal).

4.2.2. 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 $CDCl_3$.

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 [15, 16].

Solid content of the resins 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 emulsion with a mesh of 160 µm. The value presented is the ratio between the residue mass and the total resin mass.

Minimum film-forming temperature (MFT) was determined according to standard ISO 2115:1996.

Viscosity was measured using a Brookfield LV instrument, with a Spindle number 2, 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.

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.

Rubbing 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 paint film. The solvents used were xylene and propanone. The values reported are an average result for at least two test runs.

4.2.3. Solution polymerization of AcFAD

For homopolymerization, AcFAD (2 wt.%) was placed with 2 ml of toluene and 2 % (molar) of BP into a round bottom flask, equipped with magnetic stirrer, thermometer, nitrogen bubbling and a water condenser. The reaction was carried out with vigorous stirring at 85 ^{o}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.

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 round bottom flask, equipped with magnetic stirrer, thermometer, nitrogen bubbling and a water condenser. The reaction was carried out with vigorous stirring at 85 ^{o}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.

4.2.4. Emulsion copolymerization of AcFAD

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

The resin was synthesised by aqueous free radical emulsion polymerization at 80 ^{o}C, carried out in jacketed flask reactor equipped with water condenser, mechanical stirrer, thermometer and nitrogen bubbling system.

A pre-emulsion was prepared by mixing 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 ^{o}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.

Different trials were conducted by varying the surfactants and initiator concentrations, the monomers, the presence of chain transfer agent and the monomers addition process.

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 CFAs 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}) [7].

Acrylic resin (reference): **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). **^{1}H NMR** ($CDCl_3$): δ in ppm = 0.89 (6H, CH_3 from ABU and α-CH_3 syndiotactic from MMA), 1.04 (3H, α-CH_3 isotactic from MMA), 1.39 (2H, -CO-O-CH_2-CH_2-C$\underline{H_2}$-CH_3 from ABU), 1.61 (2H, -CO-O-CH_2-C$\underline{H_2}$-CH_2-CH_3 from ABU), 1.75-2.51 (2H, CH_2 of the α-methanediyl protons), 3.61 (3H, -O-CH_3 from MMA *racemic* configuration), 3.66 (3H, -O-CH_3 from MMA *meso* configuration), 4.02 (2H, -CO-O-C$\underline{H_2}$-CH_2-CH_2-CH_3 from ABU).

Acrylic resin copolymerized with 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 = 0.88 (CH_3, H_{-18} from AcFAD), 0.96 (CH_3 from ABU and α-CH_3 syndiotactic from MMA), 1.1-1.4 (α-CH_3 isotactic from MMA, 2 CH_2 from ABU, aliphatic CH_2, H_{-4}-H_{-7} and H_{-14}-H_{-17}, from AcFAD), 1.62 (CH_2, H_{-3}, from AcFAD and CH_2 from ABU), 2.04 (CH_2 allylic from AcFAD), 2.36 (CH_2, H_{-2} from AcFAD), 2.65 (CH of the α-methanetriyl protons), 2.88 (CH_2 doubly allylic from AcFAD), 3.61 (CH_3 from MMA *racemic* configuration), 3.67 (CH_3 from MMA *meso* configuration), 4.02 (CH_2 from ABU), 5.36 (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 CFAs mixture).

4.3. Results and discussion

4.3.1. Solvent homo- and copolymerization

To assess the ability of AcFAD to copolymerize, preliminary studies were performed in solution polymerization. The homopolymerization and the copolymerization of AcFAD with MMA were confirmed by NMR analyses. The results were obtained by comparing the ratio of the integrals assigned to acrylic double bonds at δ 5.76, 6.04 and 6.33 ppm (H_{-23a}, H_{-22} and H_{-23b} respectively) and to the aliphatic conjugated double bonds (at δ 6.24, 5.80, 5.51 and 5.18 ppm, (H_{-9} to H_{-12}) [8] in AcFAD and homopolymerization or copolymerization spectra.

In homopolymerization, reductions of 43 % in the area of signals of the acrylic double bonds and of 88 % in the area of the signals of the aliphatic conjugated double bonds were observed. In copolymerization both the acrylic and the aliphatic conjugated double bonds were almost completely consumed (99 %).

NMR analyses of acrylic polymers attributed the chemical shift values at δ 0.89 and 1.04 ppm as α–CH_3 syndiotactic and isotactic from MMA, respectively, allowing the identification of different polymer configurations [17, 18]. The copolymer obtained from AcFAD and MMA was 65 % syndiotactic and 35 % isotactic configurations.

These results indicates that, besides the homo- and copolymerization of AcFAD occurred by the acrylated double bonds, it also occurred involving the conjugated double bonds allowing the formation of a more resistant and crosslinked polymeric network chain.

4.3.2. Emulsion polymerization

The properties of the acrylic resin copolymerized with AcFAD, following the commercial acrylic resin formulation, were compared with the reference resin. The same quantities of the acrylic monomers without the introducing of AcFAD were used and are shown in Table 4.1. The results achieved are very similar to the control, except for the MFT, which decreased about 9 ^{o}C, showing that presence of AcFAD had a plasticization effect.

Table 4. 1 – Properties of emulsions formulated according to a commercial acrylic formulation: reference and emulsion with AcFAD as comonomer.

	Reference emulsion	**Emulsion with AcFAD (10 wt.%)**
pH	8.2	8.3
Viscosity (mPa·s)	32.5	26.4
MFT (ºC)	15.0	6.5
Solid content (%)	42.6	43.9
Filtration residue (%)	1.1	2.6

However, complete incorporation of AcFAD in the acrylic resin was not achieved, as demonstrated by the presence of a yellow supernatant liquid. This occurred probably due to inefficient emulsification of highly hydrophobic AcFAD by the surfactant used in the commercial acrylic emulsion formulation (an ethoxylated alkyl sulphate). AcFAD is still acting as a plasticizer in the dry film, but is not incorporated in the acrylic polymer chains.

Improvement of AcFAD copolymerization efficiency was attempted based on existing literature for emulsion polymerization involving a linolenic acid derivative [19]. The parameters changed were: surfactants and initiator concentrations, type of main monomers (MMA/HEMA or MMA/BA), presence of chain transfer agent, and monomers addition procedure (as a monomer mixture or as a pre-emulsion). The different approaches followed are summarized in Table 4.2.

The initial formulation (resin A) contains 6 wt.% of each surfactant, MMA/HEMA as primary monomers group, 1.45 wt.% of initiator, 3 wt.% of chain transfer agent and monomers were added as a mixture. The characterization results are presented in Table 4.2. In resin B, HEMA was replaced by BA (in the same proportion) while the other parameters were kept constant. The results with resin B (Table 4.2) were similar to the

Table 4. 2 – Optimization and characterization of the acrylic emulsion formulation using 10 wt. % of AcFAD as comonomer.

	Resin reference	**Resin A**	**Resin B**	**Resin C**	**Resin D**	**Resin E**	**Resin F**	**Resin G**
Ethoxylated alkyl sulphate	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Benzenesulfonic acid dodecyl sodium salt (wt.%)	0.0	6.0	6.0	6.0	6.0	3.0	2.0	1.5
Fatty alcohol ether sulfosuccinate disodium sal (FAES) (wt.%)	0.0	6.0	6.0	6.0	6.0	3.0	2.0	1.5
HEMA/ Methyl methacrylate (wt.%)	0.0	34.2	0.0	0.0	0.0	0.0	0.0	0.0
Methyl methacrylate/ Butyl acrylate (wt.%)	34.2	0.0	34.2	34.2	34.2	34.2	34.2	34.2
AcFAD (wt.%)	0.0	10	10	10	10	10	10	10
Initiator (wt.%)	0.3	1.45	1.45	1.45	0.2	0.2	0.2	0.2
Chain transfer agent (wt.%)	0.0	3.0	3.0	0.0	0.0	0.0	0.0	0.0
Pre-emulsion	Yes	No	No	Yes	Yes	Yes	Yes	Yes
Theoretical solid contents (%)	46	25	25	46	46	46	46	46
Viscosity (mPa·s)	32.5	19.6	21.1	30.5	39.5	58.4	59.1	36.2
Solids contents (%)	42.6	24.3	22.3	42.1	39.0	38.9	42.4	31.3
Filtration residue (%)	1.1	1.4	1.1	0.4	0.4	0.9	1.3	6.4

ones obtained for resin A, showing that HEMA may be replaced by the same amount of BA without significant change in the final properties of the emulsion.

The base formulation chosen has higher solid content (46 wt.%) than the literature formulation (25 wt.%) [19], therefore new emulsions were prepared with similar solid content. Since removal of the chain transfer agent did not affect the resin properties, the monomers were added in a pre-emulsion to produce resin C. The results showed an increase in solids content and viscosity. The change to pre-emulsion allowed following the same methodology used in the commercial acrylic resin.

Another aspect considered in the formulation optimization was the reduction of the excessive amount of surfactant used; the initial concentration of 6 wt.% was based on a literature formulation [19]. Thus, three emulsions were prepared with 3 wt.% (resin D), 2 wt.% (resin E) and 1.5 wt.% (resin F) surfactant concentrations. The results showed that the amount of surfactant cannot be reduced below 2 wt.%, otherwise AcFAD is not efficiently emulsified and copolymerized. This was confirmed by the increase of the residue value to 6.4 % and by the reduction of the solid content to 31.3 % in resin F. The results obtained with resin E agree with the reference values with the exception of viscosity. This formulation was the one that provided the most promising performing emulsion and the one chosen for the optimal formulation.

The surfactants combination (dodecyl benzene sulfonic acid sodium salt – DBSA - and fatty alcohol ether sulfosuccinate disodium sal - FAES) used during the resin optimization were determinant to emulsify either the monomers, either the polymer formed. The combination of surfactants with different hydrophilic – lipophilic balance (HLB) values is often used and suggested [14, 20 - 23].

4.3.2.1. Characterization of optimized acrylic emulsion

As shown in Table 4.2, the results obtained for resin E were similar to the commercial acrylic resin. On the other hand, the MFT for resin E was significantly lower (decreased from 15 ºC to -3.3 ºC), due to an intrinsic plasticization effect associated with the presence of long aliphatic side chains from AcFAD. This originates higher segment mobility through increased intermolecular distance [24], and avoids the need for coalescing agent additives.

Both resins were stable showing zeta potential values lower than -30 mV, specifically, -95 mV for the reference resin and -83 mV for resin E. Emulsions with zeta potential values between -30 mV and + 30 mV are most often unstable and prone to coagulate unless a steric stabilization mechanism is present [21].

AcFAD copolymerization with MMA and ABU was confirmed by NMR (Fig. 4.1) and the chemical shift values were attributed according to the poly(methyl acrylate) (PMA) and poly(methyl methacrylate) (PMMA) values giving in the literature [17, 18, 25, 26]. Comparing the spectra of the resin copolymerized with AcFAD (Fig. 1b) and the acrylic resin (reference) (Fig. 4.1c) the followed differences were observed: the appearance 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.

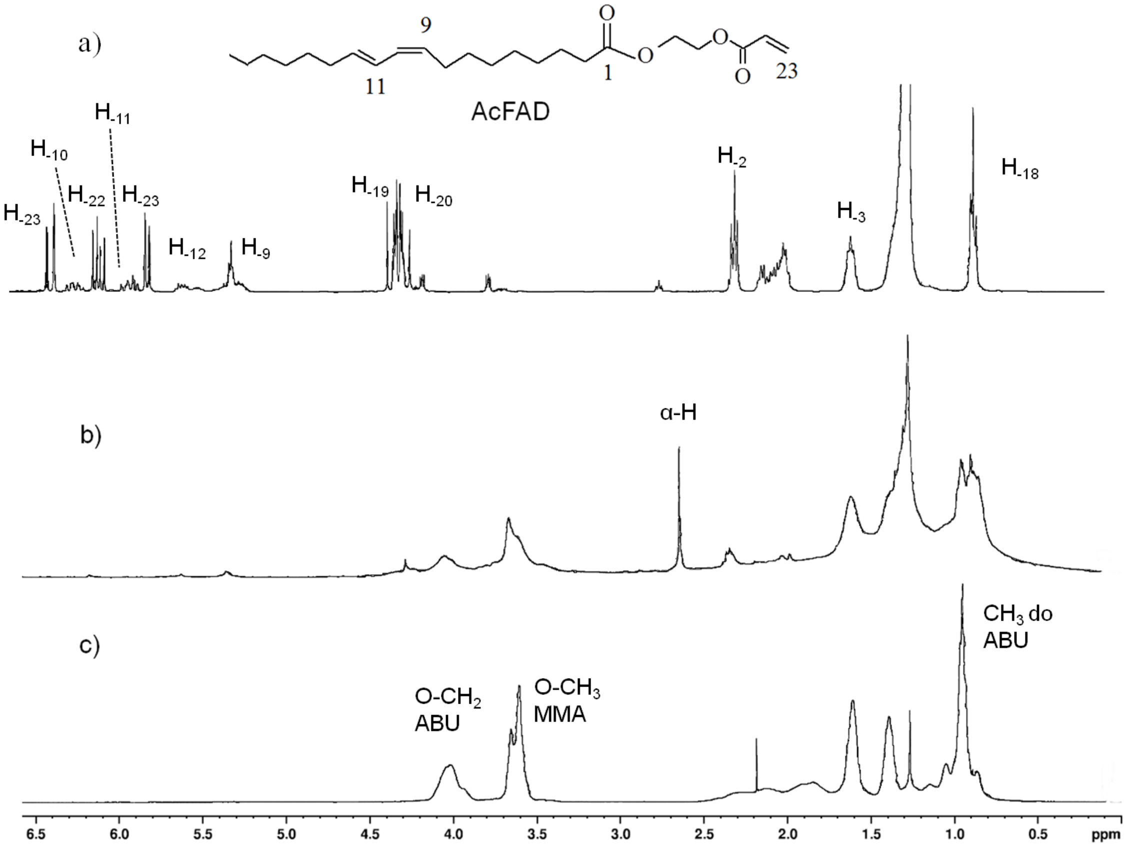

Fig. 4. 1- ^{1}H-NMR spectrum of a) AcFAD, b) resin copolymerized with AcFAD and c) reference acrylic resin.

On the other hand, a signal at δ 1.62 ppm assigned to H_{-3} (-C$\underline{H_2}$-CH_2-C(=O)-) of AcFAD (which is not present in the reference resin) 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 [27]. Due to the low amount of AcFAD present (only 10 % molar of AcFAD was added and the fraction of CFA in the commercial CFA mixture used is 50 % [7]), 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 resin 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 the oxidative cure.

To evaluate the oxidative cure behavior (since NMR allowed to identify double bonds) of the acrylic resin formulated with AcFAD as comonomer, the gel content was determined for resin E and compared with the reference acrylic resin. The films were dried for five weeks and the results (Fig. 4.2) indicated a final gel content of 6 wt.% for the reference, and of 60 wt.% in resin E. This difference demonstrates that auto-crosslinking is present in resin E [28].

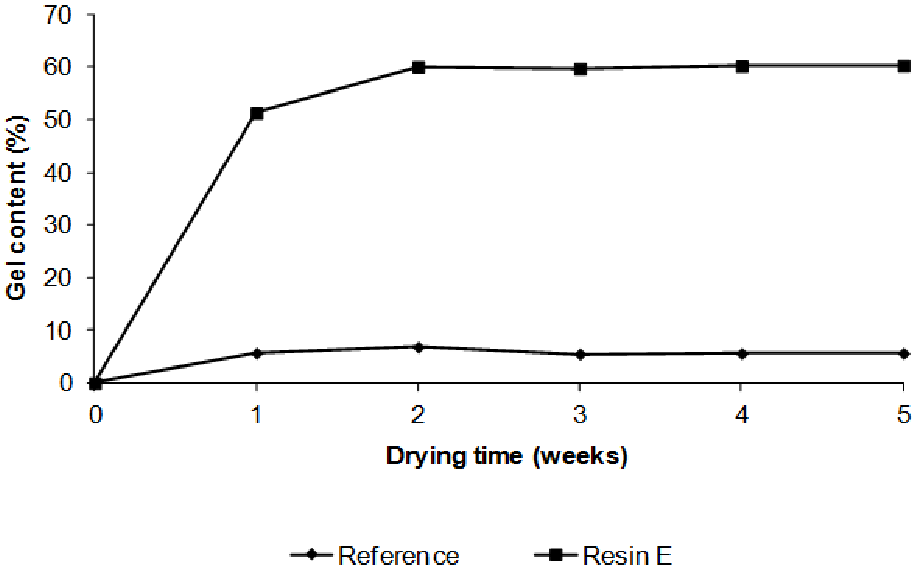

Fig. 4. 2- Gel content of resin E (copolymerized with AcFAD) and reference acrylic resin along drying time.

This phenomenon is represented in Fig. 4.3, showing the formation of peroxide bonds by reaction between the conjugated double bonds in AcFAD's aliphatic chains and atmospheric oxygen. The peroxide bond is just one example of the type of bond that can be formed on oxidative cure [7, 29].

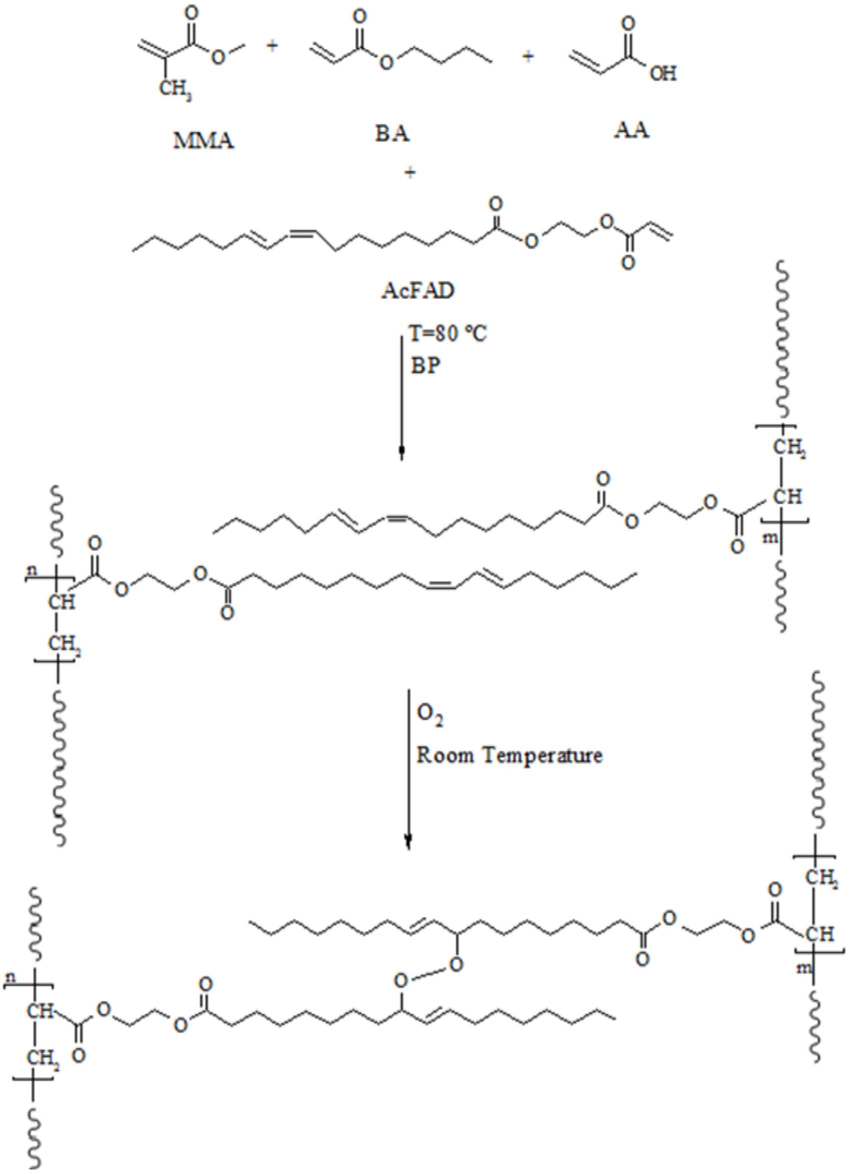

Fig. 4. 3 - Polymeric chains synthesis and crosslinking by one peroxide bond.

The oxidative cure behavior was also evaluated by FT-IR analyses in films dried in air for five weeks. Since the acrylic resin formulated with AcFAD originate a complex spectrum, causing overlapping and suppression of bands, the second derivative was applied. By comparing the second derivative spectra of the acrylic resin formulated with AcFAD after one day and after one month of drying, some differences were observed: i) slight reduction in the intensity of the bands at 2924 and 2854 cm^{-1} [symmetric and asymmetric $(CH_2)_n$], due to the hydrogen abstraction on a methylene group on the allylic position [3, 7], 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 [30, 31].

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 [7]. It was also noticed that, in films containing 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} [32].

The rubbing resistance of resin E was evaluated and compared to the reference resin (Fig. 4.4). The resistance of the emulsions to solvents of different polarities, like xylene and propanone were tested and dry films were exposed to air for up to 5 weeks. Resin E showed a higher resistance towards rubbing with xylene (Fig. 4.4a) compared to the reference resin: resin E film resisted to more 24 cycles than the reference film, which resisted to only 2 cycles.

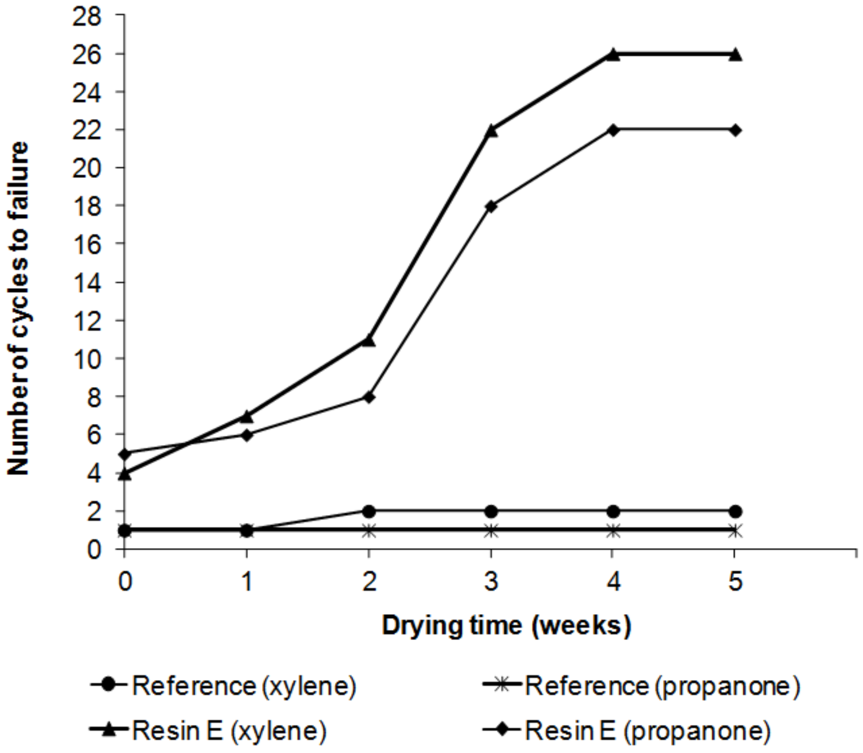

Fig. 4. 4 - Rubbing resistance of resin E (copolymerized with AcFAD) and reference acrylic resin, using a) xylene and b) propanone solvents.

Concerning the rubbing test with propanone (Fig. 4.4b) the results are similar and resin E film resisted to more 21 cycles before failure than the reference resin film, which resisted to only 1 cycle. Rubbing resistance increased during the drying time, which again confirms that oxidative cure occurs progressively, due to the presence of the AcFAD as comonomer in the new resin formulation.

4.4. Conclusions

An acrylic fatty acid derivative (AcFAD) was tested in solvent homo- and copolymerization and the final resins 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. Due to inefficient emulsification of AcFAD with the original surfactant (used in a commercial acrylic formulation), the formulation was modified until an appropriate result was obtained. NMR analyses confirmed that copolymerization occurred, involving the acrylic double bonds, and maintaining a significant number of unsaturations. The resistance to solvents (xylene and propanone) and the gel content increased significantly for the resin containing AcFAD. These results and also 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 resin with AcFAD.

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. These may be 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.

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Chapter 5

CHAPTER 5 - Low VOC self-crosslinking waterborne acrylic coatings incorporating fatty acid derivatives

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Abstract

High gloss acrylic waterborne coatings free of volatile coalescing agents were produced and characterized. The film-formers used in the coatings were resins incorporating an allyl fatty acid derivative (AFAD) and an acrylic fatty acid derivative (AcFAD), either as reactive (non-volatile) coalescing agents or as comonomers. The minimum film-forming temperatures of the new coatings were lower than the reference, confirming that AFAD and AcFAD act as coalescing agents. On the other hand, the observed reductions in through drying-time and increase in rubbing resistance, more evident for AcFAD, indicating that reaction between the conjugated double bonds in the fatty acid derivatives and atmospheric oxygen – oxidative cure – took place and provided an effective self-crosslinking drying mechanism.

Keywords: Fatty acid derivatives; Water-borne acrylic resins; Oxidative cure; Coalescing agent

5.1. Introduction

Acrylic waterborne coatings usually include in their formulation pigments, fillers, water, multi-purpose additives, and film forming components. The latter, commonly referred to as binders or vehicles, are aqueous polymer dispersions (or latexes) that are responsible for binding the pigments and fillers and forming a homogeneous film with good adhesion to the substrate [1]. Each coating formulation has a characteristic minimum film-forming temperature (MFT), which must be below the ambient temperature at which the coating is intended to dry. It is usually necessary to add coalescing agents to lower the MFT and obtain good film properties under all application conditions. These are low molecular weight compounds that act as plasticizers, softening the polymer particles and providing formation of a homogeneous and continuous film [2, 3]. After evaporation of these additives, the film hardens and a non-tacky surface is obtained.

However, current environmental regulations restrict the emissions of volatile organic compounds (VOC) into the atmosphere. Thus, coatings and varnishes industries are forced to replace volatile additives with non-volatile substances [4, 5]. Coalescing agents are an example of VOC in paint formulations and their removal implies developing formulations capable of not only coalescing uniformly, but also possessing a hardening mechanism not dependent on evaporation of additives. The introduction of self-crosslinking agents, as homo-polymers, comonomers or even as non-polymerized reactive additives is a possible strategy [6, 7]. Over the last years several studies have been done in this area, including the modification of unsaturated vegetable oils by the addition of acrylic, vinyl and styrene functions [8-13].

Self-crosslinking compounds have in their structure double bonds that can be easily attacked by atmospheric oxygen, allowing for the formation of crosslinked hardened films. During this oxidative cure and throughout the life service of the film, fatty acid auto-oxidation leads to the formation of hydroperoxides [15-17].

Fatty acid derivatives are good examples of self-crosslinking agents [17]. In this study, acrylic resins were modified with an allyl fatty acid derivative (AFAD) and an acrylic fatty acid derivative (AcFAD). Their performance in waterborne high gloss acrylic coatings was evaluated.

5.2. Experimental

5.2.1. Materials

Sunflower oil-derived conjugated fatty acids (CFA), a commercial acrylic polymer emulsion, ethylene glycol, xylene, benzoyl peroxide (BP), methyl methacrylate (MMA), butyl acrylated (BA), acrylic acid (AA), dodecyl benzene sulfonic acid sodium salt (DBSA), fatty alcohol ether sulfosuccinate disodium sal (FAES), sodium persulfate, dibutyltin oxide and all other raw materials used to synthesize the latexes were kindly supplied by Resiquímica - Resinas Químicas, S.A. (Mem Martins, Portugal). Allylic alcohol, phosphorus trichloride and acryloyl chloride were purchased from Fluka; petroleum benzin and diethyl ether from Merck; dichloromethane, anhydrous magnesium sulphate ($MgSO_4$) and anhydrous calcium chloride ($CaCl_2$) from Panreac. Triethylamine, drying catalyst (a combination of 3 % cobalt, 3 % barium and 5 % zirconium) and all the other raw materials used for the coatings formulations, were kindly provided by CIN – Corporação Industrial do Norte, S. A. (Maia, Portugal). All chemicals were used as received.

5.2.2. Characterization methods

Solid content of the resins was determined by evaporating the water in pre-weighed dishes in an oven at 105 ºC for 1 hour. An average value of 40.5 % was found.

Minimum film-forming temperature (MFT) was determined according to standard ISO 2115:1996.

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.

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 and weighed until constant weight, in order to determine the amount of insoluble crosslinked material [18]. The samples were air dried along 5 weeks. The values reported are an average for at least three determinations.

Rubbing resistance test consisted 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 paint film. The solvents used were xylene and propanone. The values reported are an average result for at least two test runs.

Gloss was measured according to standard procedure ISO 2813. Coating films with 150 µm wet thickness were applied on glass plates and allowed to air dry for 24 h. Gloss was measured at 60º, using a gloss meter, and is expressed in gloss units.

Drying time was determined by applying 100 µm film thickness on 10 cm x 15 cm glass plates, at 23 ºC and measuring the time until the surface was dry. Finger pressure was applied on the paint film and the presence of finger prints was also assessed.

For the block resistance test, 200 µm wet thickness coating films applied on 6 cm x 6 cm charts were air dried for one week. The surface of two painted squares were then put in contact and hold under a 5 kg block during 15 min in an oven at 50 ºC. After that, the squares were detached and the films appearance was evaluated.

Mixtures of 5 wt. % AFAD or AcFAD with acrylic resin were prepared by mixing the resin under vigorous stirring for 30 min. Films were then obtained by doctor-blading on a glass surface and drying at room conditions.

5.2.3. Fatty acid derivatives synthesis and copolymerization

Allyl fatty acid derivative (AFAD, Fig. 5.1) was obtained by indirect esterification of CFA with allylic alcohol. CFA was charged into a reactor with nitrogen purge, thermometer and water condenser, and heated to 60 ^{o}C. Phosphorous trichloride was added very slowly under constant stirring for 1 h. The reaction product was then cooled to 10 ^{o}C and allylic alcohol was added dropwise for 45 minutes [11].

Acrylic fatty acid derivative (AcFAD, Fig. 5.1) was also synthesized by indirect esterification of CFA with an acrylic derivative. CFA was charged into a reactor with nitrogen purge, thermometer and water condenser, and heated at 200 ^{o}C in the presence of dibutyltin oxide. Ethylene glycol was added dropwise for 2 h. The reaction product was mixed with dichloromethane and triethylamine at room temperature. Acryloyl chloride and dichloromethane were added dropwise for 2 h [19].

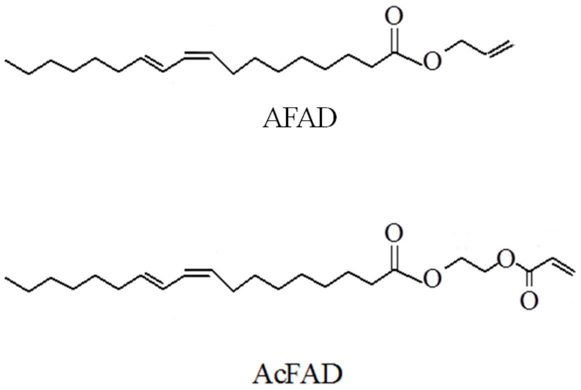

Fig. 5. 1– Allyl fatty acid derivative (AFAD) and acrylic fatty acid derivative (AcFAD) structures.

Acrylic resins used for coatings formulations were synthesised by aqueous radical emulsion polymerization, incorporating the synthesized fatty acid derivatives as comonomers. Pre-emulsion was prepared by mixing water and surfactants under vigorous stirring, followed by the addition of the monomers (MMA, BA, AA and AFAD or AcFAD), added slowly for 1 h.

The remaining surfactants and water were charged into the reactor equipped with a water condenser, a mechanical stirrer, thermometer, nitrogen bubbling and heated at 80 ºC. Simultaneously, the pre-emulsion previously prepared and the sodium persulfate (previously dissolved in 10 ml of water) were fed dropwise into the reactor over a period of 2h. The resins formulations are shown in Table 5.1.

Table 5. 1– Resins formulations**.**

	Resin with 5 wt.% of AFAD	**Resin with 5wt.% of AcFAD**
Sodium persulfate	0.2	0.2
DBSA	1.0	1.0
FAES	1.0	1.0
Methyl methacrylate	17.1	17.1
Butyl acrylate	17.1	17.1
Methacrylic acid	1.8	1.8
AFAD	5.0	0.0
AcFAD	0.0	5.0
Water	53.7	53.7
Others	3.1	3.1

5.2.4. Coating formulations

A high gloss waterborne acrylic coating formulation was used for all paints produced (shown in Table 5.2). The reference paint was formulated with an acrylic polymer resin and with conventional (volatile) coalescing agents. Paint A is similar to the reference but no coalescing agents were added. In paints B and C, AFAD and AcFAD, respectively, were incorporated as additives in the paint formulation, in order to evaluate their effect as reactive coalescing agents; no other coalescing agents were added. Finally, in paints D and E, AFAD and AcFAD were used as comonomers in the acrylic resin synthesis, in order to evaluate the effect of their presence on the resins oxidative cure. As with B and C, no conventional coalescing agents were added. All the coatings were produced following the same procedure as for the reference paint, keeping the final solids content constant. The mixtures were vigorously stirred with a high speed-mixer at room temperature and were left to rest for 24 h. Oxidative cure catalysts, also called driers, were added in all formulations where AFAD or AcFAD were present, and the mixtures stirred for homogenization.

Table 5. 2– Coating formulations.

	Resin (wt.%)			**Titanium dioxide (wt.%)**	**Thickeners (wt.%)**	**Fatty acid derivatives added as additives**		**Others* (wt.%)**
	Acrylic copolymer	**Acrylic copolymer with AFAD**	**Acrylic copolymer with AcFAD**			**AFAD**	**AcFAD**	
Reference	61	0	0	21	2	0	0	16
Paint A	61	0	0	21	2	0	0	16
Paint B	61	0	0	21	2	5	0	11
Paint C	61	0	0	21	2	0	5	11
Paint D	0	61	0	21	2	0	0	16
Paint E	0	0	61	21	2	0	0	16

* - Water and additives (Coalescing agents, biocides, anti-foaming, control pH agent).

5.3. Results and discussion

5.3.1. Acrylic resins copolymerized with AFAD and AcFAD

Some relevant properties of the acrylic resins synthesized with AFAD and AcFAD as comonomers are presented in Table 5.3 and compared with the reference resin (same proportion of acrylic monomers, but no fatty acid derivative added). All properties are similar for the three resins, except for the minimum film-forming temperature (MFT) values, which are significantly lower when either AFAD or AcFAD are present. This is due to an intrinsic plasticization effect, associated with the presence of aliphatic side chains. This leads to reduction of chain stiffening through increased intermolecular distance [20].

Table 5. 3– Resins characterization.

	Acrylic copolymer	**Acrylic copolymer with AFAD**	**Acrylic copolymer with AcFAD**
pH	8.2	8.0	8.5
Viscosity (mPa.s)	32.5	30.2	59.1
MFT (ºC)	15.0	-2.2	-3.3
Solid content (%)	42.6	41.6	42.4
Zeta Potential (mV)	-95	-72	-83

Additionally, all the resins were stable, showing zeta potential values well below -30 mV. Emulsions with zeta potential values between -30 mV and + 30 mV are usually unstable, tending to form agglomerates and sediment [21].

The gel content was determined for the three resins along five weeks drying time. The results are presented in Fig. 5.2. The commercial resin showed less than 6 % gel content. The acrylic resins copolymerized with AFAD and AcFAD had gel contents of about 48 % and 60 %, respectively, due to occurrence of oxidative cure. The difference between the two comonomers can be explained considering that with the acrylic derivative (AcFAD) polymerization takes place mostly through the acrylic double bond, and the aliphatic conjugated double bonds remain free for oxidative cure in side chains. On the other hand, the double bond in the allylic group of AFAD is much less reactive and copolymerization will then consume part of the aliphatic double bonds, decreasing the number of sites available for oxidative cure upon resin drying. [22, 23].

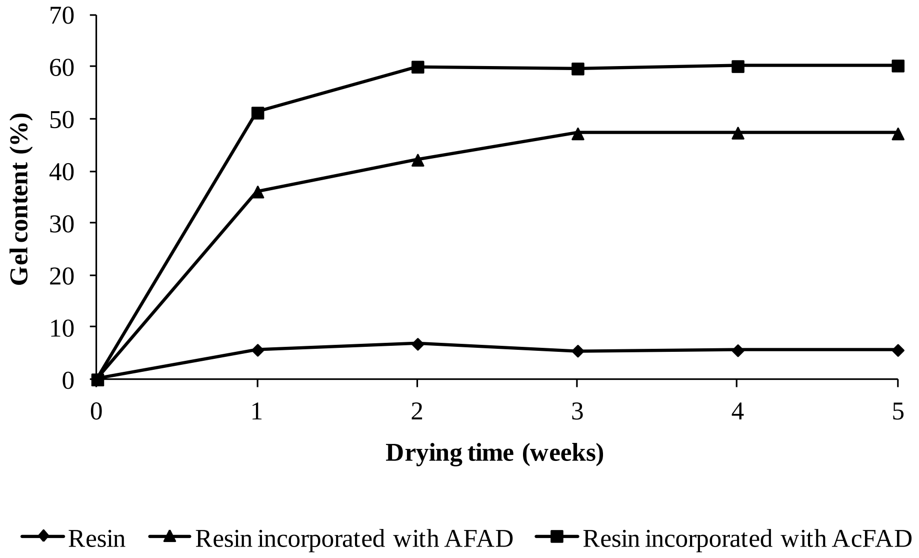

Fig. 5. 2– Gel content of acrylic resins and acrylic resins incorporating AFAD and AcFAD.

The effect of AFAD and AcFAD on rubbing resistance was determined for the resins copolymerized with AFAD and AcFAD, and compared with the reference acrylic resin. Xylene and propanone, two solvents with different polarities, were used in the rubbing cycles, during a 5 week period. The rubbing test with xylene (Fig. 5.3a), showed better performance for the resins modified with AFAD (22 cycles to failure) and AcFAD (24 cycles to failure). The increase in the rubbing resistance occurs along drying time, confirming that oxidative cure occurs progressively. For the rubbing test with propanone (Fig. 5.3b), the results were qualitatively similar, but failure occurred earlier. The higher affinity of the acrylic resin towards a polar solvent like propanone weakens the rubbing resistance.

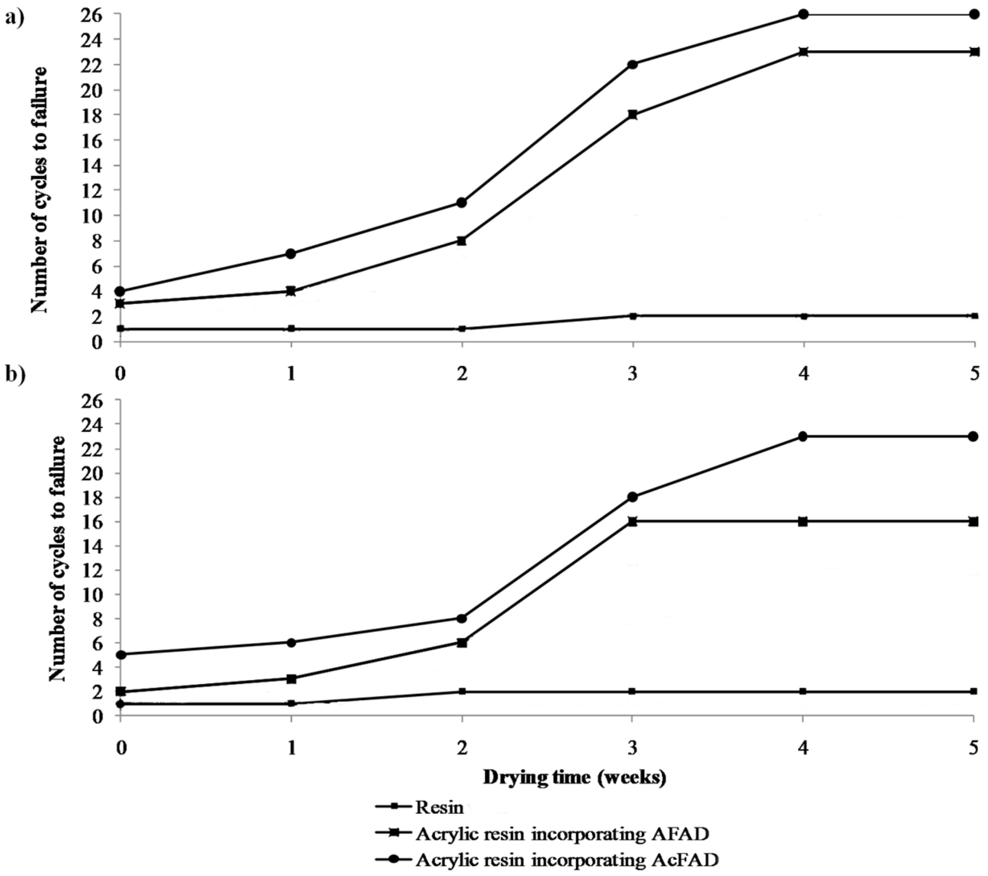

Fig. 5. 3– Rubbing resistance of acrylic resins and acrylic resins incorporating AFAD and AcFAD with driers, using xylene a) and propanone b).

5.3.2 Paint formulations

All the formulated coatings were left to rest for 24 h after preparation. Films were then applied on glass substrates and characterized after 48 h drying. Relevant properties are presented in Table 5.4 and Figure 5.4. Whiteness and yellowness indexes of all formulations (not shown here) were similar to the reference paint.

Table 5. 4– Properties of dry films obtained from coatings A to E.

	Gloss (60 º)	**MFT (ºC)**	**Blocking [1]**
Reference	75.6	-2.0	++
Paint A	79.5	11.7	++
Paint B	71.0	-3.9	++
Paint C	62.0	-3.3	++++
Paint D	60.7	-3.6	+++
Paint E	60.6	-4.1	++++

[1] + Low blocking resistance; +++++ High blocking resistance.

Paint A shows similar gloss, block resistance and through-dry time as the reference. However, as expected, the minimum film-forming temperature (MFT) is significantly higher (reference: -2.0 ºC and paint A: 11.7 ºC) due to the absence of coalescing agents. Paints B and C also do not contain conventional coalescing agents, but 5 wt. % of AFAD or AcFAD were mixed in the latex, respectively, in order to evaluated their role as reactive coalescing agents [11, 19].

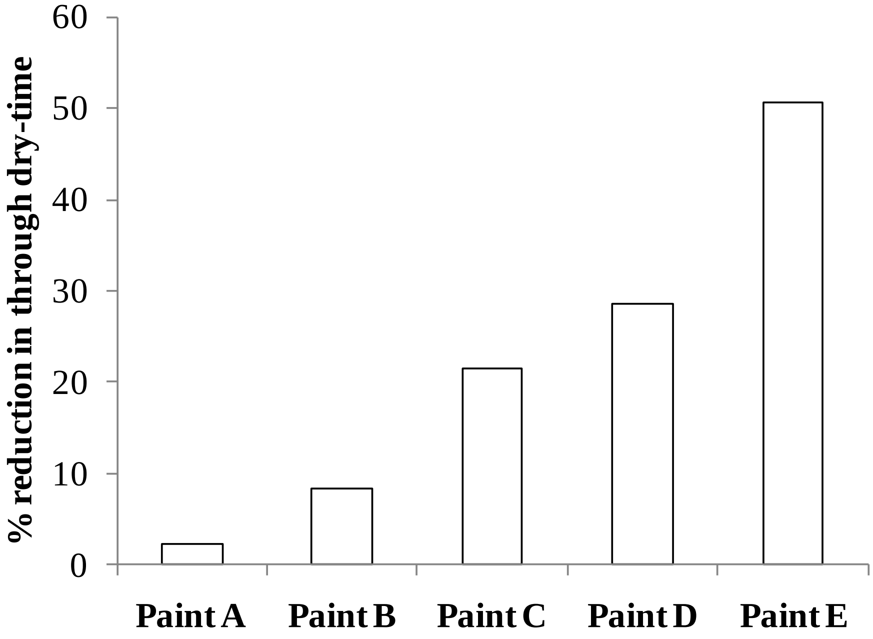

Fig. 5. 4– Reduction in through-drying time for paints A-E relative to the reference. The through-dry time for the reference was 107 min.

Paint B shows slightly lower gloss than the reference but exhibits a slight reduction in through drying-time (8.4 %) and slightly lower MFT (-3.9 ºC compared to -2.0 ºC – reference paint). Reduction in drying time is an evidence of self-crosslinking [24]. The fact that MFT is low, despite the absence of conventional coalescing agents, indicates that AFAD is also acting as coalescing agent. Paint C, containing the additive AcFAD, shows similarly low MFT and a larger reduction in through drying time (21.6 %) when compared to the reference. Gloss decrease is however more noticeable in this case. This may be associated to a competitive effect between film formation and oxidative cure. As the degree of crosslinking is higher for this paint, the polymer hardens at a faster rate, impairing coalescence. This originates a less smooth film surface with lower gloss. Block resistance of paint C is significantly better, which is associated to the higher extent of oxidative cure as indicated by the drying time result; higher film hardness leads to reduced tack. To confirm the oxidative cure NMR and FT-IR analysis were made, however, both studies were inconclusive.

Paints D and E, have AFAD and AcFAD as comonomers in the acrylic resin both these paints also show low MFT values. Reductions in through drying-times (28.6 % and 50.6 %, respectively) are much higher than for any of the previous formulations. The results for paints D and E are very dissimilar and can be explained, as discussed before, based on the different amount of conjugated double bonds available in side chains for oxidative cure.

The rubbing resistance of the applied coatings was evaluated using solvents with different polarities: xylene and propanone. The dry films were exposed to air for 6 weeks. With xylene (Fig. 5.5a), both paints E and D exhibited increasingly better performance than the reference (22 and 16 cycles to failure, respectively), as oxidative cure progressed until the fourth week. As expected from the previously discussed results, paint E consistently showed the best resistance.

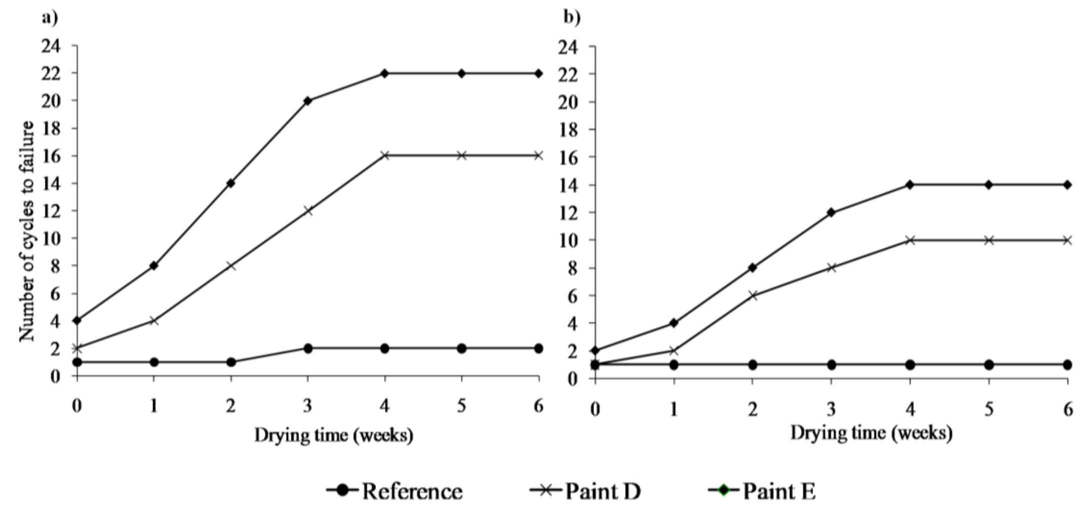

Fig. 5. 5– Rubbing resistance of paints using xylene a) and propanone b).

As previously discussed for the co-polymerized acrylic resins, the rubbing test with propanone showed the same qualitative behaviour (Fig. 5.5b), but the results with both paints were worse than with xylene.

5.4. Conclusions

An allyl fatty acid derivative (AFAD) and an acrylic fatty acid derivative (AcFAD) were tested as both reactive coalescing agent and comonomers for formulation of low VOC coatings with no addition of volatile coalescing agents. In both situations, evidences of coalescence and oxidative cure were found, but much more significantly when AFAD and AcFAD were added as comonomers. Reduction in through-drying times indicated that oxidative cure, induced by reaction between the atmospheric oxygen and the conjugated double bonds, took place. This was more evident for AcFAD. The minimum film-forming temperatures for all formulations were appropriately low, being even slightly lower than for the reference formulation, which indicates that the fatty acid derivatives also possesses a coalescing effect on the resin drying process.

Rubbing resistance tests reinforced the conclusions that oxidative cure occurred when the fatty acid derivatives were incorporated in the acrylic resins. Solvent resistance consistently increased during four weeks time as self-crosslinking proceeded within the polymeric film. Also in this case, AcFAD yielded better results than AFAD.

The incorporation of AcFAD in acrylic resins enables the formulation of high performance paints without the use of volatile coalescing agents, therefore contributing to reduce VOC emissions. This effect is stronger when AcFAD in incorporated in the resin as a co-monomer and not just as an additive (reactive coalescing agent).

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Chapter 6

CHAPTER 6 – General Conclusions and Future Work

6.1. General Conclusions

The research described in this thesis resulted in the synthesis of two compounds, AFAD and AcFAD, derived from fatty acids, presenting promising characteristics for the development of water-based high performance paints. The introduction of these compounds, either as reactive coalescing agents or as comonomers in the polymeric film-former component, introduces a self-crosslinking mechanism in the paint (oxidative cure), which allows for film hardening without the need for volatile coalescing agent. This leads to substantial reduction in VOC emissions to atmosphere and to improved film properties.

The allyl and the acrylic (AFAD and AcFAD, respectively) were synthesized by a different CFA two-step esterification: i) the conjugated fatty acid reacts with phosphorous trichloride and the intermediate reactive product reacts with an alcohol leading to AFAD; ii), the CFA reacts with ethylene glycol, followed by the esterification with acryloyl chloride, leading to AcFAD. After the synthesis optimization, both AFAD and AcFAD were characterized by FT-IR and NMR, which allowed confirming the presence of conjugated double bonds.

After addition of the synthesized fatty acids derivatives as reactive coalescing agent to a water-based acrylic resin, the results showed that the MFT decreased significantly, from 15 ºC (reference resin) to 0 ºC and -2 ºC, respectively for AFAD and AcFAD. Rubbing resistance tests of the resin dry films, using xylene and propanone, indicated performance improvements and provided evidence of progressive occurrence of oxidative cure involving the conjugated double bonds.

AcFAD polymerization in solution and emulsion was attempted. The final resins were analysed by NMR and the results showed that both for homo- and copolymerization in solvent, the polymerization reaction occurred involving the acrylic double bonds (around 50 % were consumed) and the conjugated double bonds (about 90 % were consumed). In emulsion polymerization the acrylic double bonds were totally consumed.

A water-based acrylic resin formulation was optimized in order to allow incorporation of AFAD and AcFAD as comonomers. Rubbing resistance and gel content tests confirmed the occurrence of oxidative cure in the resins containing either AFAD or AcFAD. Better results were obtained with AcFAD. Furthermore, the MFT values were considerably lower for the resins with AFAD (-2 ºC) and AcFAD (- 3 ºC) than for the reference acrylic resin (15 ^{o}C).

Finally, the paints produced with AFAD and AcFAD, both as non-volatile additives and comonomers, showed that, the MFT decreased considerably, when compared with the reference paint, indicating the coalescence effect of AFAD and AcFAD. On the other hand, the occurrence of oxidative cure was evidenced by decreases in through-drying times and improvements in rubbing resistance. Better results were obtained with AcFAD.

6.2. Future work

During the development of this work many difficulties were encountered, mainly in monomers synthesis process, in its incorporation in acrylic resins, and in paints production. Thus, as future work, it would be important to:

1. Optimize the AFAD and AcFAD synthesis processes. Different approaches could be study, namely:

    i) Replace some of the reagents involved in the synthesis, especially PCl_3, which releases HCl during the reaction and requires some storage and environmental precautions. This would allow for a more friendly process.
    ii) Maintain the CFA as raw material but substituting the other reagents, transforms the process of two steps esterification, into one step esterification.
    iii) Replace the CFA for drying oils, via a transesterification reaction or use commercial epoxy oils for functionalization with acrylic function.
    iv) In all procedures, it would be important to identify yield losses and possible strategies to minimize them. Finally, to increase the yields and

reproducibility, it would be interesting to implement on-line FT-IR, which would allow for monitoring the reactions involved in the synthesis process.

2. Continue the study of paints production:

Optimize the incorporation of AFAD and AcFAD on formulations of high gloss water-based paints. The studies performed so far have shown that gloss decreases when the acrylic resin is modified with the fatty acid derivatives. Alternatively, incorporation may be studied for matt or semi gloss paints.