Progress in Organic Coatings 81 (2015) 101–106

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Eco-paints from bio-based fatty acid derivative latexes

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ARTICLE INFO

Article history:
Received 28 October 2014
Received in revised form
15 December 2014
Accepted 4 January 2015
Available online 23 January 2015

Keywords:
Coatings
Paints
Fatty acids
Miniemulsion polymerization
Renewable resources

ABSTRACT

A series of fatty acid derivative latexes has been incorporated as binders in waterborne paints: methacrylated oleic acid (MOA) and methacrylated linoleic acid (MLA) homopolymers and copolymers of the petroleum derivative monomer methyl methacrylate and its structurally analogous renewable resource monomer α-methylene-γ-butyrolactone. The performance of the resulting paints has been evaluated in terms of hardness, gloss, rheological behaviour and open time and the final properties have been compared with a commercial waterborne paint. Most of the prepared paints showed good performance properties, making these compounds good candidates for their use in the production of sustainable waterborne paints.

1. Introduction

Solvent-borne paints typically contain high levels of volatile organic compounds (VOC) and have been traditionally used on wood and metal surfaces, providing a high gloss finish but associated to longer drying times and strong odour [1]. In contrast, waterborne paints have lower levels of VOC. In view of the detrimental effect of the release of VOC to the atmosphere, since 1970, government regulation [2,3] and the efforts of the paint industry have dramatically reduced the environmental impact of paints. Thus, nowadays, many companies offer waterborne paints equivalent to solvent-borne paints but having lower levels of VOC. The advantages of a waterborne paint include faster drying times, less odour and easier cleaning up.

Generally, waterborne paint formulations contain polymer latexes as binders to hold the film together and supply coating integrity, pigments that provide the paint with colour and covering power, thickeners that are viscosity modifiers to achieve a good pseudoplastic behaviour, wetting agents to reduce the surface tension of the coating facilitating substrate wetting and also aid pigment particles to be wet by binder and/or dispersants to prevent flocculation of the pigment particles [1].

The polymer latex accounts for about the 50% of the total weight, so it governs in large extent the properties of the coating film and the application method. Therefore, the choice of binder is of paramount importance. The use of acrylic polymers as binders have been extensively exploited in paints since they provide the coating with good properties such as good exterior durability, UV stability, film clarity or heat and alkali resistance [1]. Nevertheless, these petroleum derivative polymers do not comply with the requirement of being a renewable source material.

In the last two decades, a great amount of research is been devoted to the production of waterborne coatings based on renewable oil resources [4] such as waterborne alkyds [5,6], alkyd-acrylic hybrids [7–9], alkyd-acrylic blends [10,11] and oil modified polyurethane dispersions [12]. Alkyd resins were introduced in the 1930s as binders for paints. Alkyds are a very versatile binder so that they are widely used in architectural, industrial or decorative coatings. Like alkyd resins, fatty acids, which account for the 95% of the total weight of the vegetable oils, are valuable precursor because they present carbon–carbon double bonds and carboxylic groups as reaction sites that allow the easy incorporation of different functional groups making them suitable for a broad range of applications. Even though fatty acids are key components of alkyd resins as they can be made by condensation polymerization of fatty

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http://dx.doi.org/10.1016/j.porgcoat.2015.01.001
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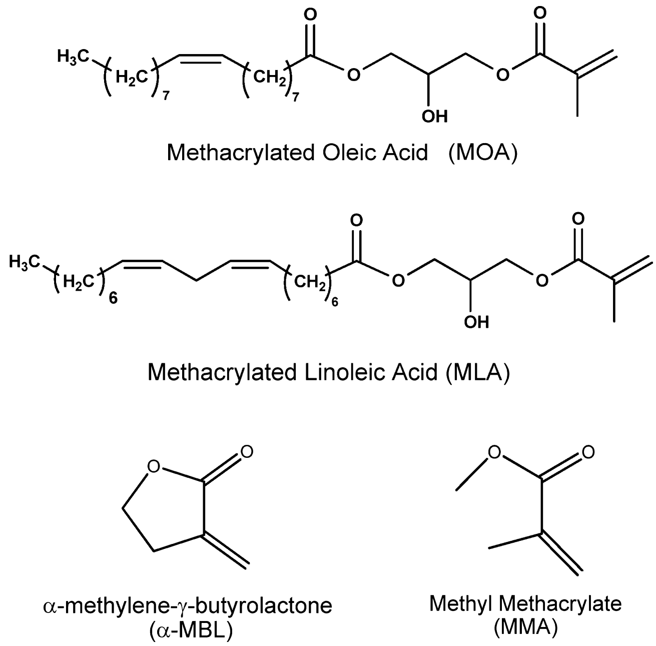

Fig. 1. Chemical structure of the used monomers.

acids, to date, the use of fatty acid-based polymers in coatings is not very expanded.

Fatty acids bearing non-conjugated double bonds are not reactive enough to undergo effective free radical polymerization. The incorporation of a (meth)acrylate moiety can make them reactive. Indeed, recent contributions have shown that methacrylated fatty acids, such as oleic acid (OA) and linoleic acid (LA) derivatives can be polymerized via free radical polymerization in aqueous media. Miniemulsion polymerization was demonstrated to be an appropriate technique to polymerize these hydrophobic monomers because, contrary to emulsion technique, polymerization occurs mainly in the monomer droplets and therefore there is no need for monomer diffusion through the water phase [13–15]. The resulting latexes presented colloidal and mechanical properties comparable to the petroleum based acrylic latexes, so their use as binder for coatings could be envisaged [16,17].

The first objective of this work was to evaluate the performance of the methacrylated oleic acid (MOA) and methacrylated linoleic acid (MLA) derived latexes as potential binders for coatings. The renewable resource monomer α-methylene-γ-butyrolactone (α-MBL), which can be found naturally in several plants such as Artabotrys odoratissimus and tulips [18,19], and the petroleum derivative monomer methyl methacrylate (MMA), which is very often used in waterborne binders and it is the non-cyclic analogous of α-MBL, were used as comonomers. For this purpose, the glass transition temperature (T_g), the minimum film forming temperature (MFFT), the gloss and the open time of MOA and MLA-derived homopolymers and copolymers were measured. The second objective was focused on the incorporation of the previously synthesized fatty acid-derivative latexes into paint formulation. The resulting paints were evaluated and their properties compared with a commercial waterborne paint used as decorative paint, in terms of hardness, gloss, rheological behaviour and open time.

2. Experimental part

2.1. Latexes used as binders

MOA and MLA-derived homopolymer and copolymer latexes with 30 wt% and 45 wt% solids contents (SC) were evaluated as binders for paints. Specifically, MOA and MLA homopolymers and MOA and MLA copolymers with α-methylene-γ-butyrolactone (ratio 85/15 wt%, and named MOA–MBL and MLA–MBL respectively) were analyzed. Furthermore, copolymers with MMA (fatty acid/MMA 85/15 wt%, named MOA–MMA and MLA–MMA) were also evaluated. The reason behind choosing this copolymer ratio is that those copolymers have glass transition temperatures at around room temperature (as it will be shown in Section 3.1.1). See chemical structures in Fig. 1. The latexes were synthesized by batch miniemulsion polymerization as it is described in our previous works [16,17]. Potassium persulfate (KPS) was used as initiator in the case of 30%SC latexes. The 45%SC latexes synthesized with KPS were very viscous, likely due to the formation of potassium oleate or other oligomers soluble in the aqueous phase that enhanced its viscosity [20]. Thus, high solids contents polymer latexes synthesized with tert-butyl hydroperoxide/ascorbic acid (TBHP/AsA) as initiator were also prepared, resulting in low viscosity latexes. All the reactions were carried out at 70 °C.

Tables 1 and 2 present the characteristics in terms of conversion and final particle size of the low and high solids contents latexes used within this study, respectively.

Table 1
Main characteristics of 30%SC latexes.

Sample	Conversion (%)	d_p (nm)
MOA	100	184
MOA–MMA	99	151
MOA–MBL	98	203
MLA	96	155
MLA–MMA	95	127
MLA–MBL	94	110

Table 2
Main characteristics of 45%SC latexes.

Sample	Initiator type	Conversion (%)	d_p (nm)
MOA	KPS	99	206
MOA–MMA		98	161
MLA		95	–
MLA–MMA		99	165
MOA	TBHP/AsA	99	183
MOA–MMA		97	151
MLA		98	180
MLA–MMA		97	150

Table 3
Mill base formulation.

Ingredient	Name	Amount (g)	wt%
Water	Demi water	114.45	22.89
Dispersant	Disperbyk 190	18.4	3.68
Pigment	Tiona 595	367.15	73.43

2.2. Preparation of waterborne paints

Waterborne paints from fatty acid-derivative latexes were prepared by using a standard formulation for decorative paints, in a two-step process. First of all, the mill base (formulation in Table 3) was prepared by mixing the dispersant (Dysperbik 190, BYK Chemie) and water in a tin, while stirring at about 400 rpm using a high speed disperser blade (HSD, DISPERMAT). The pigment (TiO_2, Tiona) was added slowly into the tin and the shear rate was increased up to 1300 rpm during the TiO_2 addition. Then the polymer latex was incorporated to the mill base. Finally, the thickener (Acrysol RM2020, 2.0 wt%) to adjust paint viscosity and a drier (BORCHI OXY COAT that contains iron bispidon complex) were added. Paints containing the 45%SC latex were formulated as