Challenges to incorporate high contents of bio-based isobornyl methacrylate (IBOMA) into waterborne coatings

Oihane Llorente, Aitor Barquero [*], María Paulis, Jose Ramon Leiza

POLYMAT, Kimika Aplikatua saila, Kimika Fakultatea, Universidad del País Vasco/Euskal Herriko Unibertsitatea UPV/EHU, Joxe Mari Korta zentroa, Tolosa hiribidea, 72, 20018 Donostia, Spain

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ABSTRACT

Emulsion polymerization of (meth)acrylic bio-based monomers is a promising method to obtain waterborne coatings with reduced carbon footprint. However, the high hydrophobicity of some bio-based monomers can hinder the straightforward incorporation of such monomers in waterborne dispersions. In this work, we explore the copolymerization of bio-based isobornyl methacrylate (IBOMA) with 2-octyl acrylate (2-OA) to produce latexes with >70 % bio-content suitable for coating applications. First, the homopolymerization of IBOMA is studied to gather more information on the emulsion polymerization of the monomer producing high Tg polymer with different surfactants. It is found that the batch emulsion homopolymerization of IBOMA is challenging due to coagulation during the polymerization, likely as a result of mass transport limitations due to the high hydrophobicity of IBOMA. Interestingly, stable dispersions are achieved when 5 % of the IBOMA is substituted by methyl methacrylate. The stability of the IBOMA/2-OA copolymer system is found to be dependent on both the IBOMA concentration in the copolymer and the solids content of the latex. Thus, we provide a stability map for IBOMA/2-OA copolymers with different compositions and solids contents showing the areas where stable and not-stable dispersions are obtained.

1. Introduction

Waterborne (meth)acrylic polymer dispersions are widely used for many applications such as coatings and adhesives. They have an excellent water and UV resistance, making them a better alternative than vinyl acetate [1] or styrene [2] for many coating applications. The existence of a wide variety of acrylic and methacrylic monomers is one of the advantages of (meth)acrylate monomer systems, together with the fact that the copolymerization between them allows a great flexibility in properties such as glass transition temperature or hydrophobicity of the copolymer. Industrially, the most common ones are the alkyl chain esters, including methyl methacrylate (MMA), n-butyl acrylate (BA) or 2-ethylhexyl acrylate (2-EHA). Moreover, there is a broad library of functional monomers bearing (meth)acrylic groups such as phosphate, amine, silane, epoxy or the acids themselves that can be easily copolymerized with the alkyl ester monomers to produce copolymers with special functionalities.

The most relevant industrial polymerization technique to produce waterborne dispersions is emulsion polymerization, as it is used to produce about 10 % of the total polymers worldwide [3]. It is generally considered an environmentally friendly process, due to the lack of solvents and the mild conditions that are required [3]. However, with the increasing environmental concerns this is not enough. Although emulsion polymerization is already a relatively green process, the carbon footprint of the product can be decreased even more if the origin of the raw materials is the biomass instead of petroleum [4]. In this context, the use of partially or fully bio-based monomers to substitute the traditional oil-based monomers is a great option. There are many bio-sources to obtain monomers, such as carbohydrates, terpenes, lignin derivatives and vegetable oils [5–8]. However, not every monomer that can be produced from biomass is viable. In order to be a real alternative for the industrial implementation, the performance given by these new monomers should be at least as good as the current monomers, and they cannot be excessively more expensive [9,10].

Industrially, the easiest strategy to substitute the oil-based (meth) acrylic monomers by their bio-based counterparts is to obtain monomers with similar chemistry and properties, so they can be directly implemented in the already developed processes [11]. One possible method is to produce (met)acrylate esters by the esterification of oil-based acrylic or methacrylic acid with bio-based alcohols to obtain acrylate or

methacrylate monomers that are partially bio-based [12,13]. To maximize the bio-content of monomers produced by this method, an interesting strategy is to increase the number of carbon atoms in the bio-based alcohol as much as possible, taking into account that a minimum solubility of the monomer is necessary for emulsion polymerization. Following this path, we focused our research on two monomers that are gaining attention: isobornyl methacrylate (IBOMA) and 2-octyl acrylate (2-OA), both of them commercially available and with a respective bio-based content of 71 and 73 % (based on carbons) [14–24]. IBOMA is produced by esterification of methacrylic acid with bio-based camphene, synthetized by a catalytic isomerization of α-pinene, which can be extracted from many plant sources, especially pine trees [25,26]. On the other hand, 2-OA is obtained from esterification of acrylic acid with bio-based 2-octanol [27,28], which is produced from the cracking of ricinoleic acid, a major component of castor oil [29].

Isobornyl methacrylate is a monomer with a homopolymer of a high Tg (literature values range from 140 to 195 °C) [30,31], and can potentially be used to substitute methyl methacrylate or styrene in waterborne formulations. It is used in many patents for the production of coatings [32,33] and pressure sensitive adhesives [34–36], and in the open literature too. However, there are examples that show that the direct substitution of MMA by IBOMA is not straightforward. Fang et al. evaluated IBOMA as a direct alternative to MMA in pressure sensitive adhesives (PSA) based on copolymers with n-butyl acrylate, and found differences in the microstructure of the copolymers, having higher gel content and lower soluble molar mass when IBOMA was used [15]. The differences in the microstructure, combined with the different Tg of the polymers significantly affected the adhesive properties, showing that some adjustments are necessary. Using the same monomer system (IBOMA-BA) Chen et al. reported that when high amounts of IBOMA are used, the system coagulated [20]. They attributed this behavior to the high hydrophobicity of IBOMA, which reduced the adsorption of the surfactant, weakening the colloidal stability of the system. Other researches did not report stability issues when using IBOMA, although arguably the IBOMA content in those cases was lower [14,16–18,22].

On the other side, poly(2-octyl acrylate) has a Tg of −44 °C, and therefore it is a potential alternative to either n-butyl acrylate or 2-ethyl-hexyl acrylate. Although 2-OA has been extensively used in patents, few works can be found in the open literature. The most exhaustive work was done by Badía et al., where they developed mostly PSAs not only with 2-OA but also with IBOMA as main monomers [12,13,16,22,37,38]. They also showed that to substitute the traditional MMA/2-EHA system by the bio-based IBOMA/2-OA pair, adjustments in the amount of chain transfer agent (CTA) were necessary in order to get similar properties. The homopolymerization of 2-OA was studied in more detail by Barrenetxe et al., and they found that 2-OA was more prone to branching and crosslinking reactions than 2-EHA when both monomers were homopolymerized under the same conditions [39].

2-OA and IBOMA have also been used for coating applications. Indeed, this is a very interesting approach because they are more hydrophobic than their traditional oil based counterparts (BA and MMA, respectively). Hydrophobicity is a much desired quality for many applications, but especially for coatings, as the water resistance plays a key role. This makes these monomers interesting beyond their greener origin, as the performance can be better. Gonzalez et al. used the IBOMA/2-OA pair to produce coatings by miniemulsion polymerization with excellent anticorrosive properties [19]. Allasia et al., on the other hand, compared the polymerization of oil-based MMA/BA monomers with bio-based IBOMA/2-OA using a methacrylated casein as stabilizer [24]. An interesting remark of their work is that when they tried to polymerize the bio-based system, they could not achieve any conversion unless small amounts of MMA (≤5 %) were added. They attributed this to the low monomer concentration in the aqueous phase due to the high hydrophobicity of IBOMA and 2-OA and the mechanism of nucleation in this surfactant-free emulsion polymerization process that is strongly affected if the monomer concentration in the aqueous phase is negligible.

Semibatch emulsion polymerization is the industrially most relevant technique to produce polyacrylates, but there is no example in the open literature of the synthesis of an IBOMA/2-OA copolymer by this method that will produce a polymer suitable for coatings. To obtain such a copolymer (with a Tg of about 4 °C), the monomer ratio in the formulation should be around 38/62 (IBOMA/2-OA by weight %, assuming that the Tg of pIBOMA is 150 °C). However, as shown by Chen et al. and Allasia et al., obtaining a stable latex with high amounts of IBOMA can be difficult. In this work, we address the challenge of the synthesis of an IBOMA/2-OA copolymer latex with high amounts of IBOMA and high solids contents (as required for a coating application). To do this, we systematically study the effect of variables such as solids content and copolymer composition in the batch and semibatch emulsion copolymerization of IBOMA and 2-OA. Moreover, prior to the synthesis of the bio-based IBOMA/2-OA coating formulation, the homopolymerization of IBOMA will be studied in detail, testing different surfactants and polymerization methods.

2. Materials and methods

2.1. Materials

The main monomers, isobornyl methacrylate (IBOMA) and 2-octyl acrylate (2-OA) were kindly provided by Evonik industries and Arkema (France), respectively. Dowfax 2A1 (from Dow Chemical), Disponil AFX 1080 (from BASF), Sipomer PAM 200 (from Solvay), Latemul PD-104 (from KAO Corporation), Hitenol KH-10 (from DKS), Emulan OG (from BASF) and Aerosol MA-80 (from Cytec) were kindly given by their respective suppliers. Methyl methacrylate (MMA) was supplied by Quimidroga. Potassium persulfate (KPS), methacrylic acid (MAA), sodium lauryl sulfate (SLS) and sodium bicarbonate (NaHCO₃) were purchased from Sigma-Aldrich. Every chemical was used as received without any further purification. Deionized water was used in all reactions.

2.2. Polymerizations

Batch emulsion polymerizations were carried out in 100 mL bottles immersed in a water bath at 70 °C. The entire load was charged in the bottles and then they were sealed. Then, the bottles were purged with nitrogen for 10 min. After they were immersed in the bath, the bottles were tumbled end-over-end at 49 rpm for 3 h. The bottles were left to cool down to room temperature before they were characterized. 70 latex grams were prepared in each bottle. A general formulation is given in Table 1.

Batch miniemulsion polymerizations were carried out in the same setup as the batch emulsion polymerizations, but prior to the introduction of the reactant in the bottle, the mixture was sonicated for 10 min in an ice-bath in a Hielscher-UIS250V Sonicator at 100 % amplitude and 100 % duty cycle.

The semibatch emulsion polymerizations were carried out in a 250 mL jacketed glass reactor equipped with a mechanical turbine stirrer, nitrogen inlet, condenser and sampling device. The temperature of the reactor was maintained by a thermostatic bath and the feeding was

Table 1
Formulation used for the batch emulsion polymerizations.

Reactant	Amount [g]
Monomer	21
Water	49
Surfactant	Variable
KPS	0.105

controlled by a commercial software (Camile TG) connected to the feeding pumps and balances. A seeded semibatch strategy was used, where at the beginning of the reaction a preformed latex (seed) was charged to control the number of particles in the reactor. After the seed was charged to the reactor, it was heated to 70 °C and a shot of initiator (KPS aqueous solution) was added, immediately followed by the feeding of a preemulsion containing the monomers, water and surfactant for 4 h. The latex was then left for one additional hour at 70 °C to achieve full conversion. The seed was produced in the same setup (in a 1 L reactor) also by semibatch feeding of the monomer mixture during 4 h to achieve a latex of 13 % solids content (S.C.) and 80 nm particle size. The formulation of the seed and particle growth step are given in Tables 2 and 3.

2.3. Characterization

The solids content of the latex was calculated gravimetrically by weighing the latex before and after it was dried and using Eq. (1). The samples were dried in a ventilated oven at 65 °C until a constant weight was achieved.

$$S.C. = \frac{Weight\ of\ the\ dry\ material}{Weight\ of\ the\ latex} \qquad (1)$$

The instantaneous conversion at time t, x (t), was calculated from the solids content, using Eq. (2).

$$x\ (t) = \frac{(S.C.(t) \cdot L_T(t)) - NPS\ (t)}{M_0 + F_M \cdot t} \qquad (2)$$

where S.C. is the solids content as calculated by Eq. (1), L_T (t) and NPS (t) are the total weight of the latex and non-polymerizable solids (initiator, surfactant, buffer salts) at time t (in g), M_0 is the amount of monomer in the initial charge (g), F_M is the feeding rate of the monomer (g·min^{-1}) and t is the feeding time (min).

The amount of coagulum was measured gravimetrically. The latex was filtered with an 80 μm nylon mesh and the unfiltered matter was dried in an oven until constant weight was achieved.

It is worth to note that the calculation of the conversion using the solids content is not accurate when it is not possible to quantify how much coagulum is formed. Thus, for latexes with high amounts of coagulum that could not be quantified the latex yield (X_L) was calculated, as done by Tauer and coworkers [40]. X_L refers to the ratio between the solids content that was obtained in the dispersed phase after filtering at the end of the polymerization (calculated with Eq. (1)) and the maximum possible solids content (calculated from the formulation). Therefore, for high conversion latexes it will be inversely proportional to the amount of coagulum.

Z-Average particle diameters were measured by Dynamic Light Scattering (DLS). A Zetasizer Nano ZS from Malvern Instruments was used. Samples were prepared by diluting a fraction of the latex in doubly deionized water. The analyses were carried out at 25 °C and a run consisted on 2 min of temperature equilibration followed by three size measurements of 2 min each. An average value is given as a result.

Table 2
Formulation used for the synthesis of the seed.

	Reactant	Amount [g]
Initial charge	Water	686
	Dowfax 2A1	2.3
	NaHCO$_3$	1.6
Initiator solution	KPS	0.5
	Water	10
Feeding (4 h, 0.433 g·min^{-1})	IBOMA	39.5
	2-OA	64.5

Table 3
Formulation used for the seeded semibatch emulsion polymerizations with a target 40 % S.C.

	Reactant	Amount [g]
Initial charge	Seed	55.3
Initiator solution	KPS	0.4
	Water	10
Feeding (4 h, 0.575 g·min^{-1})	IBOMA	27.7
	2-OA	45.1
	Dowfax 2A1	3.1
	Water	62.1

3. Results and discussion

3.1. Batch homopolymerization of IBOMA

The batch homopolymerization of IBOMA was studied first. In emulsion polymerization, and particularly with very hydrophobic monomers, the surfactant has a crucial role in the formation and stabilization of the particles. The batch emulsion homopolymerization of IBOMA was carried out using a variety of ionic and non-ionic surfactants and combinations of them. Table 4 shows the chemical structures of the surfactants that were used and Table 5 shows the final solids content and latex yield at the end of the batch emulsion polymerizations for latexes with a target solids content of 30 %.

In every reaction high amounts of coagulum were formed. However, as poly(isobornyl methacrylate) is a very hard polymer, in some cases it was not possible to remove the coagulated polymer from the bottle, and therefore the coagulum was not quantified. A picture of the bottles with the coagulum is presented in Fig. S.1 in the Supplementary Material. Nonetheless, the visual evaluation indicated that high monomer conversion were achieved in all cases. Thus, the discussion in this section will be based on the latex yield and not the coagulation percentage.

There are clear differences depending on the type of surfactant that was used. Anionic non-polymerizable surfactants gave the best results, with latex yields above 70 % in both cases. Disponil AFX 1080, non-ionic surfactant, gave very poor results when it was used alone in concentrations as high as 5 wt%. Nonetheless, a slightly higher latex yield was obtained when the higher concentration was used.

The results of the polymerizable ionic surfactants were the worst. The reactions performed with Sipomer PAM200 and Hitenol KH-10 completely coagulated. These two surfmers are known to homopolymerize, and are partially soluble in the aqueous phase, so most likely they polymerized in the aqueous phase forming water-soluble polymer that coagulated the system by bridging flocculation. On the other hand, Latemul PD-104 gave a latex yield of 17 %, which is not good by any means but made it the best in the series with polymerizable surfactants. This is likely because this surfmer does not homopolymerize, and therefore the water-soluble polymer was not formed.

The surfactant mixtures that were tried did not improve the results. The Dowfax 2A1/Emulan OG pair performed similarly to the Dowfax 2A1 alone, suggesting that most of the stabilization was provided by the ionic surfactant. It is a bit contradictory that the mixture with higher amount of Dowfax gave a lower latex yield; however, this can be the result of small irreproducibility issues due to the instability of the system. Nonetheless, the potential irreproducibility in these polymerizations is not concerning, as all reactions failed in a higher or lower degree. Last, in the case of Disponil AFX 1080/Aerosol MA-80 pair it is clear that a more stable latex is obtained with a higher concentration of the ionic surfactant.

Chen et al. attributed the coagulation of the polymerizations with high amounts of IBOMA to the high hydrophobicity of pIBOMA, that decreases the surface energy of the particles and thus, reduces the adsorption of surfactant molecules [20]. This hypothesis was challenged by performing miniemulsion homopolymerizations of IBOMA using two of the most successful surfactants of the previous trial, Dowfax 2A1 and

Table 4
Chemical structures of the different surfactants used in this work.

Surfactant	Type	Structure
Dowfax 2A1	Ionic	
Sodium lauryl sulfate (SLS)	Ionic	
Aerosol MA-80	Ionic	
Sipomer PAM200	Ionic, polymerizable	
Latemul PD-104	Ionic, polymerizable	
Hitenol KH-10	Ionic, polymerizable	m = 9–11
Disponil AFX 1080	Non-ionic	R = C$_{12-14}$
Emulan OG	Non-ionic	Fatty alcohol ethoxylate (structure not available)

Table 5
Properties of the poly(IBOMA) latexes produced by batch emulsion homo-polymerization using different surfactants and a target solids content of 30 %.

Reaction	Surfactant			S.C. [%]	X$_L$ [%]
	Type	Surfactant	% wbm[a]		
IB_1	Ionic	Dowfax 2A1	1.5	25	83
IB_2	Ionic	SLS	1.5	22	73
IB_3	Non-ionic	Disponil AFX 1080	3	4	13
IB_4	Non-ionic	Disponil AFX 1080	5	7	23
IB_5	Ionic, polymerizable	Sipomer PAM200	1.5	–[b]	–
IB_6	Ionic, polymerizable	Latemul PD-104	2	5	17
IB_7	Ionic, polymerizable	Hitenol KH-10	1	–[b]	–
IB_8	Ionic	Dowfax 2A1	1.4	21	70
	Non-ionic	Emulan OG	0.6		
IB_9	Ionic	Dowfax 2A1	1	24	80
	Non-ionic	Emulan OG	1		
IB_10	Non-ionic	Disponil AFX 1080	1.4	6	20
	Ionic	Aerosol MA-80	0.6		
IB_11	Non-ionic	Disponil AFX 1080	1	23	77
	Ionic	Aerosol MA-80	1		

Note: after 12 month of storage all the latexes were coagulated.
[a] Weigh % based on monomer.
[b] Massive coagulation happened, it was not possible to measure.

SLS. Results are presented in Table 6. Note that the target solids content for the miniemulsions was 28 %, so the latex yield was calculated using this value.

The results of the miniemulsion polymerization were completely different from the emulsion, as no macroscopic coagulation was observed and latex yields above 93 % were obtained for all cases. Interestingly, this contradicts the hypothesis of Chen and coworkers, because 1 % of Dowfax 2A1 or SLS is enough to stabilize these dispersions.

The other potential explanation for the coagulation during the emulsion homopolymerization of IBOMA might be its low water solubility ($2.45 \cdot 10^{-5}$ mol·L^{-1} or $5.45 \cdot 10^{-4}$ g·100 g$_{H_2O}^{-1}$) [24]. As a result, there might be limitations in the monomer transport from monomer droplets to polymer particles that can lead to coagulation [41–43]. As noted by Schork, the addition of a more hydrophilic comonomer can enhance the solubility of hydrophobic monomers [41]. To explore this possibility, some additional polymerizations were carried out, taking as base formulation the most successful one (IB_1 from Table 3, with Dowfax 2A1 as surfactant). Inspired by the work of Allasia et al. [24], 5

Table 6
Properties of the poly(IBOMA) latexes produced by batch miniemulsion homo-polymerization using Dowfax 2A1 and SLS as surfactants.

Reaction	Surfactant		S.C. [%]	X$_L$ [%]	dp (nm)
	Surfactant	% wbm			
IB_12	Dowfax 2A1	1	26	93	312
IB_13		2	27	96	184
IB_14	SLS	1	27	96	152
IB_15		2	27	96	123

% of the IBOMA was substituted by methyl methacrylate (MMA). In a similar manner, in another reaction 1 % of the IBOMA was substituted by methacrylic acid (MAA), as it is even more water soluble than MMA. Results are presented in Table 7. The reaction performed with pure IBOMA (IB_1) is also included as reference.

Similarly to what Allasia et al. observed, the addition of a small fraction of methyl methacrylate greatly improved the polymerization of IBOMA, as the amount of coagulum was reduced from 15 % to 1 %. The result of IB_16 is comparable for those obtained by miniemulsion polymerization. On the contrary, the addition of 1 wt% of methacrylic acid increased the amount of coagulum up to a 21 %.

It seems that the addition of a more hydrophilic monomer helps to carry out the polymerization with no coagulation, but if the monomer is too hydrophilic, the beneficial effect is not observed. There is an important difference between MMA and MAA, as the methacrylic acid is water soluble, while MMA is only partially soluble ($1.5 \ g \cdot 100 \ g_{H2O}^{-1}$). Thus, it is possible that the MAA mostly homopolymerized in the aqueous phase forming water soluble oligomers that induced bridging flocculation, similarly to what was discussed for some of the polymerizable surfactants.

It is not simple to rationalize how the MMA helps on the polymerization of IBOMA. The miniemulsion polymerizations already showed that for these solids contents the amount of surfactant used is enough to stabilize the dispersion, thus, the underlying reason seems to lie on the polymerization in the water phase. The addition of 5 % of MMA to the formulation drastically changes the composition of the water phase. Using the partition coefficient of MMA (log Pow = 1.38) [44] and assuming that IBOMA is saturating the aqueous phase, 99 % of the monomer in the aqueous phase is MMA. If the lack of stability in the homopolymerization of IBOMA is a result of a lack of oligoradical formation that enters into the micelles or precipitates and absorbs surfactant, this would explain why the MMA helps, as the nucleation process will be similar to the homopolymerization of MMA. Moreover, the solubility of IBOMA is 6.5 % higher with MMA in the water phase (calculated using Yalkowsky's rule of mixing as suggested by Jouyban and Schork [41,45]), therefore improving the mass transport of IBOMA.

3.2. Batch emulsion copolymerization of IBOMA and 2-OA

The batch emulsion copolymerization of IBOMA with 2-octyl acrylate was carried out with the same methodology as the homopolymerization of IBOMA. The monomer ratio for a coating application that would yield a copolymer of a Tg of 4 °C is 38/62 (wt/wt, IBOMA/2-OA) assuming a Tg of 150 °C for IBOMA. Nonetheless, it was considered interesting to study a broader range of compositions, so copolymers with compositions from 15/85 to 40/60 were synthetized using Dowfax 2A1 as surfactant. Results are presented in Table 8.

The results of the copolymerization of IBOMA with 2-OA are significantly better than the homopolymerization of IBOMA and similar to the polymerization of IBOMA with 5 wt% of MMA (run IB_16). Full conversion and 100 % of latex yield were achieved in all cases, with a minimum amount of coagulum. Interestingly, the amount of coagulum shows an increasing trend as the concentration of IBOMA increases, but it is always below 1.5 %.

On the other hand, carboxylic acids (e.g. acrylic and methacrylic acid) functionalized latexes are sought for many applications. As observed in Table 7, MAA led to coagulation in the homopolymerization of IBOMA, but as the system with 2-OA is much more stable a new series was carried out adding 1 wt% of MAA to the formulation. Results are presented in Table 9.

As can be seen, when IBOMA is copolymerized with 2-OA the presence of MAA does not have any significant effect (neither detrimental neither beneficial) in the stability of the latexes, as the results present in Tables 8 and 9 are nearly identical. This is very different from what was observed in the homopolymerization of IBOMA, where the addition of 1 wt% of MAA led to a substantially higher amount of coagulation (Table 7).

Due to the success of the previous reactions, the solids content was increased to 40 %, as many applications require higher solids contents than the 30 % produced so far. The results are presented in Table 10.

Slightly worse results were obtained at 40 % S.C. than at 30 % S.C., but still very high latex yields were obtained, and the coagulation was below 10 % in all cases. Surprisingly, the amount of coagulum increased as the IBOMA concentration in the formulation decreased, contrary to what was observed in previous results.

3.3. Semibatch copolymerization of IBOMA and 2-OA

The semibatch polymerization is the preferred process when acrylate and methacrylate monomers are copolymerized. Not only is the control over the reaction heat much better, leading to a safer process, but also it allows producing a much more homogeneous copolymer, overcoming the differences in the reactivity ratios of acrylate and methacrylate monomers. Fig. 1 presents the time evolution of the instantaneous conversion and solids content (left) and evolution of particle size over the solids content (right) during the semibatch emulsion copolymerization of IBOMA with 2-OA in a 38/62 wt% ratio, with a final target

Table 8
Properties of the latexes produced by batch emulsion copolymerization of IBOMA and 2-OA at different monomer ratios using 1.5 wt% of Dowfax 2A1 as surfactant.

Reaction	IBOMA	2-OA	S.C. [%]	X_L [%]	Coagulum [%]	dp [nm]
IB-OA_1	15	85	30	100	0.4	115
IB-OA_2	25	75	30	100	1.2	112
IB-OA_3	30	70	30	100	1.2	111
IB-OA_4	35	65	30	100	1.4	111
IB-OA_5	40	60	30	100	1.4	107

Table 9
Properties of the latexes produced by batch emulsion copolymerization of IBOMA and 2-OA at different monomer ratios with 1 wt% of MAA using 1.5 wt% of Dowfax 2A1 as surfactant.

Reaction	IBOMA	2-OA	MAA	S.C. [%]	X_L [%]	Coagulum [%]	dp [nm]
IB-OA_6	15	85	1	30	100	0.5	120
IB-OA_7	25	75	1	30	100	0.9	128
IB-OA_8	30	70	1	30	100	1.4	122
IB-OA_9	35	65	1	30	100	1.4	119
IB-OA_10	40	60	1	30	100	2.6	119

Table 7
Properties of the latexes produced by batch emulsion polymerization of IBOMA with small amounts of more hydrophilic comonomers. The target solids content was 30 %.

Reaction	Surfactant		Composition	S.C. [%]	X_L [%]	Coagulum [%]	Dp [nm]
	Surfactant	% wbm					
IB_1	Dowfax 2A1	1.5	IBOMA	25	83	15	–
IB_16			IBOMA/MMA 95/5	28	93	1	115
IB_17			IBOMA/MAA 99/1	24	82	21	151

Table 10
Properties of the latexes produced by batch emulsion copolymerization of IBOMA and 2-OA at different monomer ratios with a solids content of 40 %, using 1.5 wt% of Dowfax 2A1 as surfactant.

Reaction	IBOMA	2-OA	Surfactant	S.C. [%]	X_L [%]	Coagulum [%]	dp [nm]
IB-OA_11	15	85	Dowfax 2A1	39	98	7.2	139
IB-OA_12	25	75	Dowfax 2A1	40	99	6.1	138
IB-OA_13	30	70	Dowfax 2A1	40	100	3.5	138
IB-OA_14	40	60	Dowfax 2A1	40	100	4.1	132

solids content of 40 %. Fig. S.2 in the Supplementary Material shows the time evolution of the particle size distribution.

As observed, very high instantaneous conversions were achieved, and the particle size grows with the solids content. It is worth noting that at the end of the process, as the solids content approaches 40 % there is a slight increase in the particle size. This can be an indication that the system is reaching the stability limit and is starting to coagulate. Nonetheless, at the end of the polymerization, only 4 % of coagulum was obtained, and all of it was collected around the nitrogen tube or thermocouple. These are the areas of the reactor with the highest shear, which might have led to that small coagulation. Therefore, despite the slight increase in the particle size at the end of the polymerization, this latex was considered to be stable. The DSC of the film obtained from drying the latex (in Fig. S.4 in the Supplementary Material) shows a clear Tg of the copolymer at 3 °C, indicating that the obtained polymer is suitable for a coating application.

The solids content of the formulation was then increased to 50 %, which is even more desirable from an industrial perspective and application. The time evolution of the instantaneous conversion and solids content (left) and evolution of particle size over the solids content (right) are presented in Fig. 2. Fig. S.3 in the Supplementary Material shows the time evolution of the particle size distribution and the formulation for the 50 % S.C. reaction is presented in Table S.1.

The polymerization was much more problematic when the target solids content was 50 %. After 120 min of reaction, the instantaneous conversion apparently starts to decrease. This is an indication of coagulum starting to form. Coincidentally, the solids content of the dispersion is 43 % at this point, which might be indicating that the stability limit of this system is around 40 % S.C. As observed in Fig. 2 (right), the increase in the particle size is even more pronounced when the solids content approximates 50 %, further indicating that the stability limit of the system is around 40–45 %. By the end of the reaction, 21 % of coagulum was collected.

Collecting all the information presented in this publication and the data available in literature [22,24], we have built an IBOMA/2-OA copolymer stability map as a function of the solids content of the latex and the IBOMA content of the copolymer. Fig. 3 presents in red the regions where non-stable latexes have been produced and in green the range of solids content and IBOMA compositions that so far yielded stable polymer latexes. The intermediate grey area represents the region where there is no experimental data and the stability of the resulting latex is unknown.
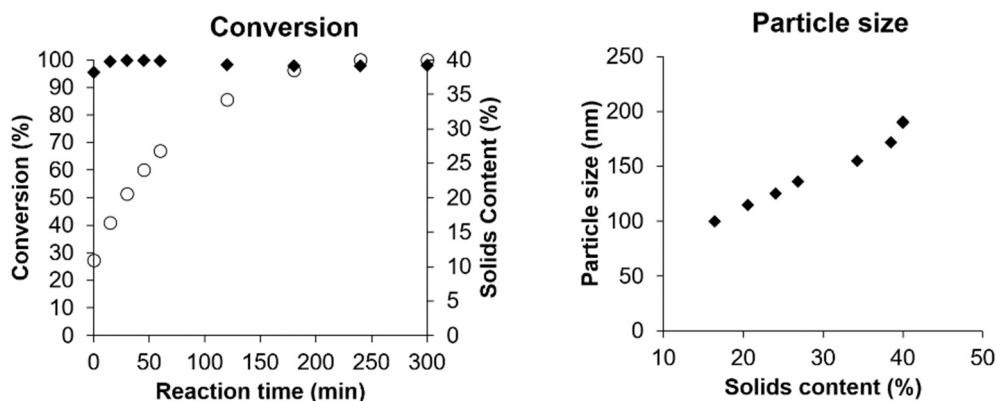

Fig. 1. Time evolution of conversion (●) and solids content (○), (left) and evolution of particle size with the solids content (right) during the semibatch emulsion copolymerization of IBOMA and 2-OA at final target 40 % solids content.
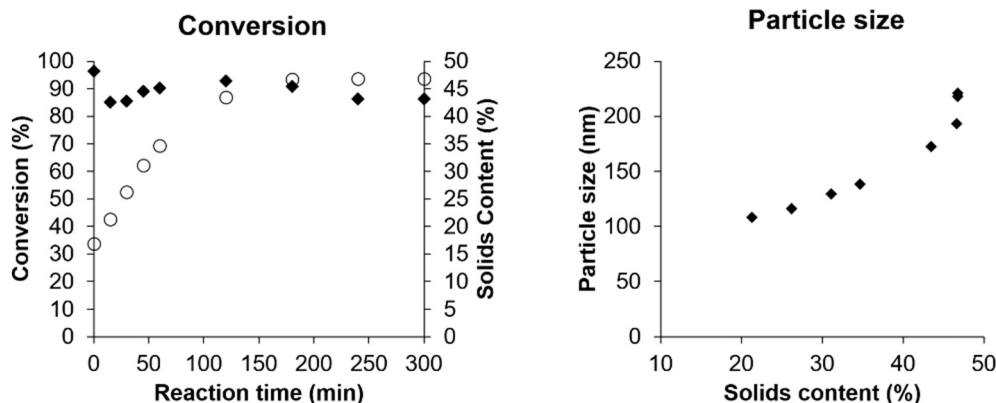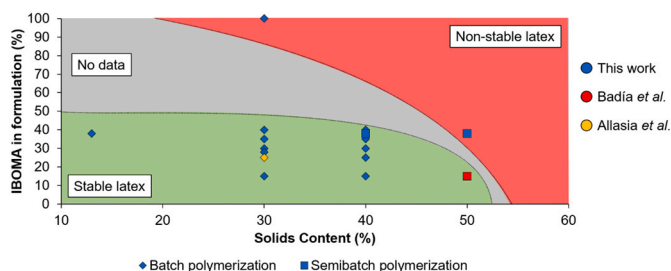

Fig. 2. Time evolution of conversion (●) and solids content (○), (left) and evolution of particle size with the solids content (right) during the semibatch emulsion copolymerization of IBOMA and 2-OA at final target 50 % solids content.

Fig. 3. IBOMA/2-OA copolymer latex stability map as a function of IBOMA content and solids content when produced by emulsion polymerization with Dowfax 2A1 as surfactant.

4. Conclusions

In this work, we have addressed the challenge of the incorporation of high amounts of bio-based IBOMA monomer in emulsion copolymerization reaction with the also bio-based 2-OA to produce bio-based copolymer latexes at high solids contents.

As a first step, the homopolymerization of IBOMA was studied, as literature reports already warned about the difficulties of producing copolymers containing high IBOMA contents. It was found that no matter the surfactant that was used, the homopolymerization always led to a coagulation of the latex. The best results were for the ionic non-polymerizable surfactant Dowfax 2A1, with 15 wt% of coagulum. Interestingly, this reaction was successful when performed by mini-emulsion polymerization, suggesting that the problems in the emulsion homopolymerization of IBOMA arise from limitations of the mass transport of the monomer through the aqueous phase. Moreover, a successful stable latex was obtained when 5 % of the IBOMA was substituted by methyl methacrylate. This was likely due to the higher hydrophilicity of MMA, that could slightly increase the solubility of IBOMA and help during the particle nucleation, but the underlying mechanism could not be fully understood. A deeper study of the polymerization in the aqueous phase and the nucleation steps will likely help to better understand this system.

Copolymerization with 2-OA was more successful and solids contents up to 40 % could be achieved in batch and semibatch processes with up to 40 % of IBOMA in the copolymer. Unfortunately, the same reaction coagulated when the target solids content was 50 %, showing that for formulations with 40 % of IBOMA the limit for a stable latex is around 40–45 % solids content. Last, we provide a latex stability map for the IBOMA/2-OA copolymer system as a function of IBOMA and solids content, that should help design new copolymers.

CRediT authorship contribution statement

Oihane Llorente: Conceptualization, Methodology, Investigation, Writing - Review & Editing.
Aitor Barquero: Investigation, Writing - Original Draft.
Maria Paulis: Conceptualization, Methodology, Writing - Review & Editing, Supervision.
Jose Ramon Leiza: Conceptualization, Methodology, Writing - Review & Editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.porgcoat.2022.107137.

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