Towards improved performance of waterborne polymer dispersions through creation of dense ionic interparticle network within their films

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ABSTRACT

To overcome the main challenge of low performance of the waterborne polymer coatings due to the particulate nature of the polymer dispersions and the complex film formation process, in this work we implemented the strategy of ionic complexation between oppositely charged waterborne polymer particles. For that aim, doubled charged ionic monomers ithaconic acid (IA) and styrenic 1,4-diazabicyclo[2.2.2]octane (DABCO) were used to densely functionalize (meth)acrylic film forming polymer particles, synthesized by seeded semi-batch emulsion polymerization to produce high solids content anionically and cationically charged polymer dispersions, respectively. The main advantage of the double charges in the selected ionic monomers is that they provide high ionic charge density onto charged particles at lower content of ionic monomers.

The blending of these oppositely, densely charged and concentrated dispersions resulted in instantaneous coagulation. To postpone the immediate complexation, water-soluble non-ionic polymeric stabilizing species as steric obstacles around the colloids were employed, which allowed to prepare colloidally stable blends and to prepare ionic complexed films. Certainly, the established ionic complexes between carboxylic acids of IA anionic monomer and quaternary ammonium groups of DABCO units within the films improved substantially the mechanical properties and the water sensitivity of the ionic complexed polymeric films with respect to individual films and the reference blend, in which ionic bonding was prevented by pH control. Moreover, the dense ionic network formed within the film actuated as a strong barrier to the leakage of all the water-soluble species during film immersion in water. Beside simple strategy towards improved performance of waterborne coatings, these results offer further extension of their application potential.

1. Introduction

Sustainable development is one of the great challenges of the 21st century. Without any doubt, this complex issue must be addressed at many different levels, including prolonging the lifetime of our equipment, vehicles and infrastructures. One of the most efficient ways of expanding the lifetime of the goods is their protection by high performance polymer coatings, usually produced by solution polymerization. Nevertheless, such solvent-borne coatings are one of the highest contributors to volatile organic compounds (VOC) released in the atmosphere. Because the sustainable development requires elimination or at least a severe reduction of the use of solvents in coatings' formulation,

the stricter legislatives pushed the coatings' producers to widely replace the solvent-borne coatings by water-borne ones, which are gaining market space worldwide.

Since the water-borne dispersions consists of individual polymer particles dispersed in aqueous medium, formation of a continuous coating film from such dispersions is a complex process comprising few stages, including water evaporation, particles packing and polymer chains interdiffusion between the adjacent particles. Consequently, the films originated from water-borne dispersions usually present much more defects, and decreased mechanical and water resistance than films produced from polymer solution [1]. There are different efforts reported for improvement of the water-borne films quality mostly based on the

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improvement of the polymer chain interdiffusion step during film formation. For example, while plasticizer addition to the polymer dispersions improve the film formation process, it simultaneously increase the VOC content [2]. Alternatively, the chains diffusivity can be improved by blending of polymer particles with low and high glass transition temperatures (T_g) [3,4] or developing multiphase systems that combine hard and soft polymer domains within the same polymer particle [5]. In both cases, while hard polymer provides mechanical strength, the soft fraction allows proper polymer chain mobility in order to complete the film formation process. Formation of covalently crosslinked polymer films is another approach that can overcome the drawbacks of the weak mechanical properties associated to waterborne polymer films. Crosslinking not only provides the coatings with mechanical stability, but also chemical resistance, high softening point and high barrier against oxygen, which are essential for certain applications [6]. As the film might be applied to different types of surface (including irregular), crosslinking has to be developed once the polymer dispersion has been deposited on the substrate. Application of crosslinking agents during film formation as carbodiimides was reported to enhance the film formation process [7]. However, these type of chemicals used in the self-crosslinking reactions are becoming under scrutiny due to their toxicity and may be banned in certain non-industrial and long-term application. One of the possible alternatives to the chemical crosslinking during film formation is the introduction of non-covalent interactions. It might be achieved either by establishing H-bonding [8], or by strong ionic interactions. Among the materials providing physical interactions, ionic bonding seems to be good candidates due to the strong electrostatic interactions that they can provide [9,10].

Recently, we have shown that by introducing ionic interactions between oppositely charged particles synthesized by emulsion polymerization of methyl methacrylate (MMA)/butyl acrylate (BA), not only the mechanical resistance of the polymeric films was increased producing stiffer films without important loss of flexibility, but also the water penetration within the polymeric films was considerably hindered [11]. Nevertheless, the mechanical reinforcement effect of the established ionic complexation between the particles was rather modest and limited by the particle surface charge density. These results suggest that by promotion of ionic interactions the performance of the waterborne coatings might be enhanced further by multiplying the ionic bonds between the particles by increasing the charge density on the particles' surface. As the particles were charged by using small amount of ionic monomers copolymerized with BA/MMA, the attempts to increase the charge density by using higher ionic monomers quantities resulted in considerable creation of water-soluble oligomers. Consequently, polymer dispersions with high ionic strength were obtained that decreased the colloidal stability and affected negatively the water resistance of the resulting polymer films.

A promising approach to overcome these challenges can be to increase the charge density without increasing the quantity of ionic monomers, which eventually can be achieved by using functional monomers that contain more than one charge per molecule. Hence, this work is focused on creation of dense ionic inter-particle crosslink network within BA/MMA waterborne polymer coating films, for first time to the best of authors' knowledge provided by synthesis of charged particles by incorporation of functional ionic monomers with two charges per molecule. For this purpose, itaconic acid (IA, Fig. 1a) was used as anionic monomer, whereas styrenic 1,4-diazabicyclo[2.2.2]octane (DABCO, Fig. 1b) was selected as the cationic one. They were copolymerized with BA/MMA (50/50 wt% ratio) main monomers by a two-step seeded emulsion polymerization process.

The incorporation of the doubly charged monomers onto polymer particles, which provides moreover colloidal stability, will be a key point to enable the study of the ionic bonding effect on the film performance. The implementation of this idea is challenging because BA and MMA as sparingly water-soluble are mainly located in polymer particles (and monomer droplets) and the double charged monomers are
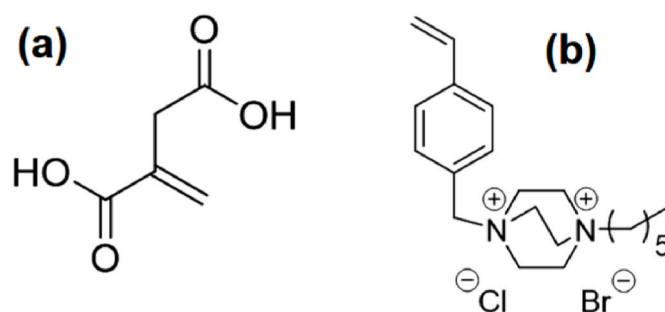

Fig. 1. Chemical structure of (a) itaconic acid anionic monomer and (b) styrenic DABCO cationic monomer.

water-soluble monomer solely located in the aqueous phase. Therefore, the system naturally tends to form polymer chains rich in ionic monomers in the aqueous phase, which due to increasing ionic strength in the system and low incorporation to the polymer particles can induce colloidal issues during synthesis and deteriorates the final polymer properties. Namely, if the concentration of water soluble oligomers rich in ionic moieties is high, the increased ionic strength in the dispersion induces shrinkage of the electric double layer that stabilizes the particles, inducing particle agglomeration and finally phase separation. Therefore, it is of great importance to control the incorporation of the water-soluble and charged monomers onto the polymer particles. However, incorporation of IA monomer onto BA/MMA polymer particles by emulsion polymerization has been scarcely studied. For instance, Oliveira et al. reported the emulsion copolymerization of BA, MMA and IA in presence of anionic emulsifier [12,13]. According to the authors, at pH around 2.7, small amount of IA anionic monomer was buried within the particles, while the remaining IA was distributed equally between the particle surface and the aqueous phase. On the other hand, we have recently reported on incorporation of DABCO cationic monomer by emulsifier-free MMA/BA emulsion polymerization performed in semi-continuous mode under starved monomer conditions to enable the incorporation and to decrease the creation of soluble oligomers in aqueous phase [14]. High solids content and film forming dispersions were attained. Following the recently developed strategy, both monomers IA and DABCO were successfully incorporated onto BA/MMA particles, providing high surface charge densities. Such dispersions were then blended to study the effect of ionic complexation between the densely charged particles on the mechanical and water resistance of the blend films. The blending process has shown to be challenging as well, because the dense ionic functionalization induced massive coagulation of the blend dispersions. This issue was resolved by addition of water-soluble polymeric species that once adsorbed onto colloids surface postponed the ionic complex induced coagulation and allowed the present study.

2. Experimental

2.1. Materials

Technical grade monomers n-butyl acrylate (BA, Quimidroga), methyl methacrylate (MMA, Quimidroga) and itaconic acid (IA, sigma Aldrich) were used as monomers. 1,4-diazabicyclo[2.2.2]octane (DABCO, Sigma Aldrich), 1-bromohexane (Sigma Aldrich), ethyl acetate ($C_4H_8O_2$), 4-vinylbenzyl chloride (90%, Sigma Aldrich) and acetonitrile (Sigma Aldrich) were used for the synthesis of the styrenic DABCO monomer. Sodium dodecyl sulfate (SDS, Sigma Aldrich) and dodecyltrimethylammonium bromide (DTAB, Sigma-Aldrich) were used as received. The initiator *tert*-butyl hydroperoxide (TBHP, 70 wt% aqueous solution, Luperox Sigma Aldrich) and Bruggolit 7 (FF7, Bruggemann Chemical) were also used as received. Polyvinyl alcohol (PVOH, Sigma-Aldrich), polyvinyl pyrrolidone (PVP, Sigma-Aldrich), and

Pluronic F-108 (BASF) were employed as polymeric/non-ionic stabilizers.

Hydroquinone (Fluka) was used to stop the polymerization reaction in the samples withdrawn from the reactor. Technical grade tetrahydrofuran (THF, Scharlab) and HPLC grade THF (Scharlab) were used for soxhlet extraction and Size Exclusion Chromatography (SEC) measurements, respectively. Hydrochloric acid (HCl, 37%, Sigma Aldrich) was used to decrease the pH of anionically charge dispersion and performed the titration analysis and sodium hydroxide (NaOH, Panreac) was employed for the titration of this anionic latex. DABCO containing dispersions were titrated using silver nitrate (AgNO$_3$, Sigma Aldrich).

To control the pH of the blends phosphoric acid (sodium) (Sigma-Aldrich) and formic acid/citric acid buffers were prepared.

2.2. Monomer synthesis

The cationic monomer DABCO is not commercially available, so prior to polymerization reaction, DABCO was synthesized following the Scheme 1, reported elsewhere [14,15], where the characterization of the monomer is reported as well.

2.3. Polymer dispersion synthesis

Ionically charged waterborne polymer dispersions were synthesized by a two-step seeded semibatch emulsion polymerization process. A typical acrylic formulation, 50/50 BA/MMA was used and IA and DABCO functional monomers were selected to give the ionic character to the latexes. In this work, in order to incorporate functional monomers into BA/MMA, the synthetic procedure developed in previous works [11,14,16] was used, however, this time the use of ionic surfactant was necessary to obtain stable latexes (SDS for anionic latex and DTAB for cationic ones).

In the first step, a seed with 50/50 BA/MMA at 10% solids content (s. c.) for anionically charged system and 20% s.c. for cationic one was prepared. Detail formulations for the seed synthesis of anionically and cationically charged waterborne dispersions are shown in Supporting Information. The desire amount of seed was loaded for the second part of the polymerizations employing BA/MMA, 1/1 by weight. While 1 wt% relative to the main monomers (BA and MMA) of IA was used for anionically charged dispersion, two different concentration of DABCO ionic monomer were used, 1 wt based main monomers% (wbm%) and 1.8 wbm%. Upon achieving the desire temperature of 60 °C, the compounds were fed in three streams: initiator redox couple aqueous solutions (FF7/TBHP) and a preemulsion containing BA, MMA, functional monomers and the respective surfactant reaching final solids content of 40%. After the feeding period (180 min), the system was allowed to react for one more hour. The formulations are presented in Supporting Information and the schematic view of the processes is illustrated in Scheme 2. These polymer dispersions were named as IA1 (when 1 wbm% IA was used with resect to MMA/BA quantity), DABCO1 (when using 1 wbm% DABCO) and DABCO1.8 (when employing 1.8% DABCO).

2.4. Polymer dispersions characterization

The monomer conversion was determined during the reactions gravimetrically, by measuring the non-volatile fraction of the dispersion at different times to follow the formation of polymer in the system. The instantaneous monomer conversion ($X_{inst.}$) is defined as the amount of polymer at time t ($m_{pol}(t)$) divided by the amount of monomer fed up to time t ($m_{mon.fed}(t)$):

$$X_{inst.} = \frac{m_{pol}(t)}{m_{mon.\,fed}(t)} \tag{1}$$

The global monomer conversion (X_{global}) is calculated as ratio of the amount of polymer and the total amount of monomer ($m_{mon.total}$) according to:

$$X_{global} = \frac{m_{pol}(t)}{m_{mon.\,total}} \tag{2}$$

The z-average particle size (d_p) is defined as the intensity weighted average hydrodynamic diameter measured by Dynamic Light Scattering (DLS) using a Zetasizer Nano Z (Malvern Panalytical, UK) equipped with a 633 nm red laser. The samples extracted from the reactor were diluted 1000 times with deionized water to prevent multiple scattering. The z-average size was derived from the measured correlation curve by Cumulants analysis.

Incorporation of functional monomers, surface charge density and ionic monomer fraction participating in the formation of water-soluble species were determined by titration of the dialyzed latexes. These latexes were diluted to 2.5 wt% solids content and dialyzed against ultrapure water by using Spectra-Por®4 membranes (Mw cut-off 12,000–14,000 Da) until constant conductivity. The dialyzed IA containing latex pH was first reduced to 2. These samples were titrated conductimetrically using Metrohm 718 stat titrino equipment against 0.005 M NaOH for IA latex and against 0.01 M AgNO$_3$ for DABCO latexes.

Ionic monomer incorporation (%) was calculated based on the initial mol added to the system as seed in equation (3).

$$(\text{ionic monomer } \%) = \frac{n_{neutralized}}{n_{initial}} 100 \tag{3}$$

where $n_{neutralized}$ is the number of moles of NaOH or AgNO3 require to neutralized the functional groups of the latexes and $n_{initial}$ is the number of moles added at the beginning for the polymerization reaction.

The surface charge density (σ) was calculated according to the following equation (4) [17]:

$$\sigma = \frac{Fn\rho R}{3w} \tag{4}$$

where F is the faraday constant, n is the number of moles of NaOH or AgNO$_3$ require to neutralize functional groups of the latex, ρ is the colloid's density, R is the radius of the latex spheres and w is the fraction of the solids content of the latex.

The fraction of ionic monomer participating in the formation of water-soluble species was calculated based on the initial ionic monomer
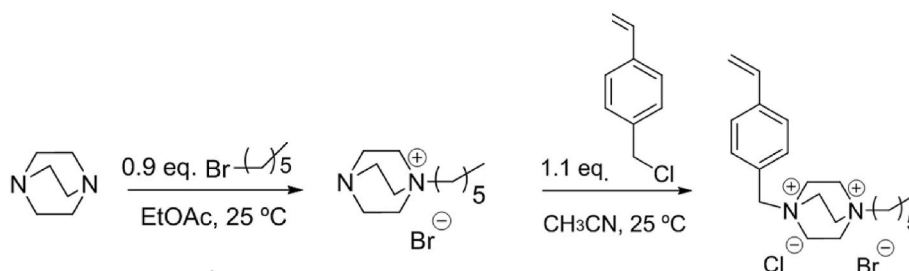
Scheme 1. Synthesis procedure of DABCO monomer.

	Initial charge	Feeding	Initial charge	Feeding
IA1	BA/MMA/IA Surfactant	1. FF7 2. TBHP	Seed (10% s.c.)	1. BA/MMA 2. FF7/IA/ Surfactant 3. TBHP

	1st step (seed synthesis)	2nd step (latex synthesis)	
t$_0$			t$_{final}$

	Initial charge	Feeding	Initial charge	Feeding
DABCO1 DABCO1.8	BA/MMA/ DABCO/ Surfactant	1. FF7 2. TBHP	Seed (20% s.c.)	1. BA/MMA 2.FF7/DABCO/ Surfactant 3. TBHP

Scheme 2. Latex synthesis procedures.

content (according to the formulation). The diluted latexes (12.5% solids content) were centrifuged at 13000 rpm for 3 h at 4 °C. The serum parts were carefully taken with a syringe and IA containing serum parts pH were reduced to 2, while DABCO containing serums were kept as taken. These samples were titrated conductrimetrically using Metrohm 718 stat titrino equipment against 0.005 M NaOH for IA latex and against 0.01 M AgNO$_3$ for DABCO ones.

The microstructure of polymer latexes were investigated measuring insoluble polymer fraction in THF and the molar masses of the soluble part. The gel content of the polymer was measured using Soxhlet extractions using tetrahydrofuran (THF) as the solvent. The gel content was defined as the insoluble fraction of the polymer in THF and the method to calculate the gel content was described elsewhere [18]. The molecular weight distributions of the soluble fractions obtained in the Soxhlet extractions were measured using size exclusion chromatography in THF at 35 °C with a flow rate of 1 mL/min. The GPC consisted of an injector, a pump (Waters 510), three columns in series (Styragel HR2, HR4, and HR6), and a differential refractometer detector (Waters 2410). The equipment was calibrated using polystyrene standards.

The glass transition temperature (T$_g$) of the polymers was determined using a differential scanning calorimeter, DSC (Q1000, TA Instruments) (Hüllhorst, Germany). The scanning cycles consisted of first cooling to −50 °C at 10 °C/min, then heating from −50 to 150 °C at 10 °C/min, cooling again from 100 to −50 °C at 10 °C/min, and then heating to 150 °C at a rate of 10 °C/min. The results from the second heating run from −50 to 100 °C will be presented herein.

2.5. Blends preparation

The main characteristic of IA is its pH dependency owing to its two pKas, pKa$_1$ = 3.85 and pKa$_2$ = 5.45 [12], while DABCO does not present any pKa value, due to the presence of the two quaternary ammonium groups. This means that when the pH of the blend is below 3.8, the IA molecules are in their molecular form preventing the ionic interactions (the blends prepared at this pH will be called reference material), whereas when the pH is higher than 5.5, anionic groups will be formed favouring the ionic complexation between the carboxylic groups presented in IA and the quaternary ammonium groups of the DABCO unit (this will be called complex material).

In order to ensure that the species contributing to the ionic bonding were coming from the surface of the polymer particles, the latexes were dialyzed against water to remove the water-soluble species and ionic surfactants from the waterborne dispersions. For this purpose, Spectra-

Por®4 membranes (M$_w$ cut-off 12,000–14,000 Da) were employed. Conductivity of water was followed until a value around 2 μS cm^{-1} was reached, which corresponds to the deionized water conductivity.

The blends were prepared by mixing both dialyzed latexes based on the equal number of opposite charges. Firstly, 1 wbm% ionic monomer (IA1 and DABCO1) containing latexes were used. As the incorporation of the DABCO into polymer particles is lower than the incorporation of IA (Table 2), more amount of DABCO containing latex was added to the blends in order to obtain equal number of oppositely charge species.

In order to increase the ionic bonding effect, blends were also performed between IA1 and DABCO1.8 containing dispersions since both latexes showed similar average particle size and surface charge density (Table 2). A summary of the prepared blends is shown in Table 1. Blends were named as Blend C indicating that the blends were performed considering the surface charge density. The numbers refer to the concentration of each latex used (IA containing latex-DABCO containing latex).

Unfortunately, despite of the addition of buffers (formic acid and citric acid/sodium phosphate) into the IA containing latex in order to decrease the pH and ensure the deprotonated state of carboxylic groups, instantaneous aggregation was obtained immediately after adding the cationic latex.

To prevent premature coagulation of oppositely charged polymer particles during blending, sterically protective polymeric species as polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVOH) and Pluronic F-108 were employed as physically absorbing protective polymers onto the IA and DABCO polymer particles [19].

Blend C1-1 and Blend C1-1.8 (Table 1) were prepared at two different pHs. At pH > 5.5, at which all the species are in their ionic state (ionic complex material) and at pH < 3.9, where no ionic interactions were expected, as IA would be in its molecular state (reference material). As pH of both polymer dispersions was 7 (the reason will be described in Results and discussion section), no buffer was employed for the ionic

Table 1
Summary of the performed blends between IA and DABCO containing latexes based on their surface charge density parameter.

	Latex (mL)	
	Blend C1-1	Blend C1-1.8
IA1	3	5
DABCO1	5	–
DABCO1.8	–	5

blend preparation, while phosphoric acid (sodium) buffer was used for the reference blend preparation to decrease the pH.

The blend dispersions were mixed for 2 h before casting into silicon molds. It should be mentioned that the pH of the dispersions was controlled during the mixing time. Furthermore, the original latexes containing either IA or DABCO were also individually mixed with the selected protective specie and dried in order to examine their final performance. These polymer films were named as IA1, DABCO1 and DABCO1.8.

2.6. Polymer films characterization

The polymer films were characterized in terms of surface morphology, mechanical properties and water resistance. The surface morphology of the films were analysed by Atomic Force Microscopy (AFM) technique. These tests were performed using a Dimension ICON AFM (Bruker) operating in tapping mode. An integrated 7 nm ratio silicon tip/cantilever with a resonance frequency of 320 KHz was used performing measurements at a scan rate of 1 Hz s^{-1} with 512 scan lines. The mechanical properties were measured by tensile tests. Tensile test measurements were performed in an universal testing machine, TA.HD plus Texture Analyser under control conditions (23 $\pm$ 2 °C and 55 $\pm$ 5% relative humidity) applying a crosshead speed of 25 mm min^{-1} to an approximate 0.6 mm film. Films with 0.6 mm thickness were prepared by casting latex into silicon molds and letting dried for 7 days under control conditions (23 $\pm$ 2 °C and 55 $\pm$ 5% relative humidity). At least five specimen per sample were analysed and the average values are reported. The water resistance was examined by water uptake test after immersion of the films in water for 1 week. The water absorption of the films was defined as the weight increase after 2 weeks, which was normalized by the initial weight of the sample.

3. Results and discussion

3.1. Characteristics of the charged polymer dispersions

The cationically and anionically charged latexes were synthesized by two-step seeded semibatch emulsion polymerization process. In the first step a seed latex was prepared that was used afterwards to synthesize the final charged dispersions in a semibatch process. The aim of the use of seed is to ensure ionic dispersions with narrow particle size distribution. On the other hand, semicontinuous process allowed performing the polymerization process at very low monomer concentration in the reactor (monomer-starved conditions) that on one hand will push forward the copolymerization between BA, MMA and IA or DABCO, independently of the reactivity ratios of all monomers. Moreover, the low concentration of monomers in the reactor decrease the secondary nucleation of new particles, contributing to the narrow particle size distribution. The main characteristics of the seed latexes and the high solids content final latexes IA1, DABCO1 and DABCO1.8 are summarized in Table 2.

According to Table 2, almost complete conversion was obtained at the end of the polymerization for both seed dispersions, reaching values above 97% with average particle size of 83 nm for IA containing latex, and 105 nm for the DABCO one (Table 2). These seeds were used to

synthesize the final high solids dispersions during the second stage polymerization. Time evolution of monomer conversion (global and instantaneous) with the two different functional monomers and different concentrations in case of DABCO are presented in Fig. 2a.

In all the cases, the instantaneous conversion during the reactions was above 95% (Table 2), confirming low monomer concentration in the reactor, which is a condition to push forward the copolymerization between BA/MMA and IA or DABCO and to eliminate the effect of reactivity ratios of the monomers on the copolymer composition, simultaneously decreasing the possibility of new particles creation due to secondary nucleation. Although there are some works in the literature stating that the presence of functional monomers as IA can slow down the polymerization [12], we did not observed any differences for different functional monomers. Very similar average particle size of around 156 nm was obtained for the both ionic monomers and for different DABCO concentrations (Table 2), which is rather low and probably result on the high ionic concentration due to the double charges in each molecule. The comparison of experimental and theoretical evolution of the particle sizes (Fig. 2b) confirmed that the seed particles were grown accordingly and that there was no secondary nucleation and coagulation (see SI for the calculation of the theoretical d_p). The lack of secondary nucleation is likely due to the low monomer concentration kept during the seeded semibatch emulsion polymerization process.

The surface charge characteristics of the polymer latexes are presented in Table 2. Even though higher monomer incorporation was obtained for DABCO1 (40–45 wt% functional monomer) than for IA1 (35% functional monomer), DABCO1 latex presents lower surface charge density. This is based on the important difference of the functional monomers' molar masses, as the ionic monomer incorporation was calculated in wt%, (IA monomer 430 g mol^{-1} and DABCO 130 g mol^{-1}). The non-incorporated ionic monomers, likely contributed to the formation of water soluble oligomers.

The surface incorporation of DABCO slightly increased from 40 to 45% with increase of cationic monomer concentration in the formulation (from 1 wbm% to 1.8 wbm%) due to the higher ionic strength in the dispersions, causing shifting the adsorption equilibrium towards the polymer particles [16]. Thus, the surface charge density was almost doubled (from 6 μC cm^{-2} for DABCO1 to 10 μC cm^{-2} for DABCO1.8). Higher DABCO incorporation did not affect the kinetics, particle size evolution and the final particle size of cationic latexes, likely because even at the lowest DABCO concentration the attained incorporation was sufficient to stabilize colloidally the system under the conditions studied.

The polymer microstructure was analysed by determining the gel content (THF insoluble polymer fraction) and the molar mass of the THF soluble part of the polymer, considering that the gel content represent crosslinked and branched polymer structures. In the present case, the gel fraction will represent as well the polymer chains that contains ions, as they are insoluble in THF, too. As observed in Table 2, IA and DABCO containing latexes present a significant amount of insoluble polymer, above 48%. The presence of ionic species in the polymer chains and the formation of physical bonds (hydrogen bonding for example in case of IA containing chains) might contribute to the formation of THF insoluble polymer [16,20], both processes with high probability to contribute to

Table 2
A summary of the latexes' characteristics.

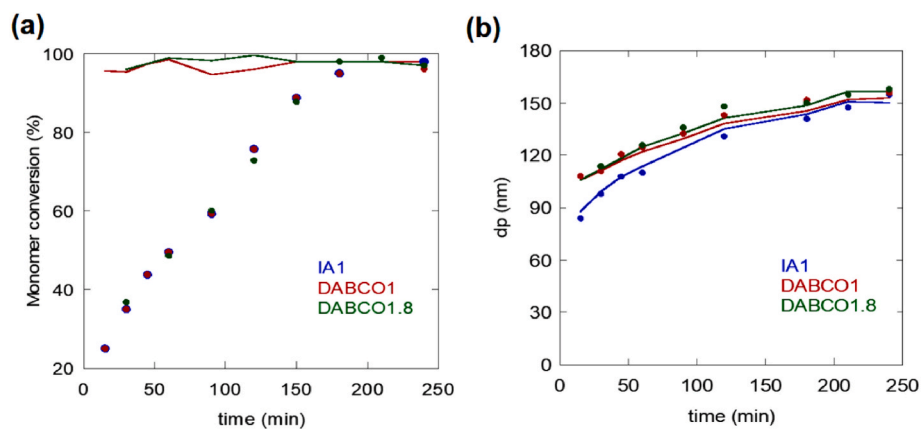| Latex	Conversion (%)	d_p (nm)	IM[a] fraction incorporated onto particles (%)	Surface charge density (μC cm^{-2})	Gel content (%)	M_w (kDa)	Ð
Seed IA	98	83 $\pm$ 1	–	–	–	–	–
Seed DABCO	97	105 $\pm$ 2	–	–	–	–	–
IA1	98	155 $\pm$ 1	35 $\pm$ 1	13 $\pm$ 1	48 $\pm$ 1	346 $\pm$ 5	2.4 $\pm$ 0.3
DABCO1	97	156 $\pm$ 2	40 $\pm$ 6	6 $\pm$ 1	55 $\pm$ 1	316 $\pm$ 2	2.4 $\pm$ 0.2
DABCO1.8	97	158 $\pm$ 2	45 $\pm$ 3	10 $\pm$ 1	50 $\pm$ 2	340 $\pm$ 3	2.5 $\pm$ 0.4

[a] IM – ionic monomer.

Fig. 2. Time evolution of monomer conversions (a) overall (dots) and instantaneous (continuous lines); and (b) average particle size of anionically and cationically charged latexes, experimental (dots) and theoretical (continuous lines).

the high gel content observed. The molar masses were in the expected range considering the emulsion polymerization process (Table 2). As expected, the molar mass decreases for higher gel fractions, since higher molecular weight chains were incorporated into the gel. The polydispersity index values were in a range of commonly obtained in BA/MMA emulsion polymerizations [11,21].

3.2. Preparation of polymer dispersion blends

Due to densely charged particles in the dispersions, after blending of positively and negatively charged latexes an immediate coagulation occurred. To avoid it, formic acid and citric acid/sodium phosphate buffers were used to control the pH during latex blending in attempts to keep the IA containing species in protonated form. Even though the pH was kept bellow pK_as of IA (5.45 and 3.85) to retain the carboxylic groups (-COOH) protonated, the blends again coagulated instantaneously. There are few possible causes behind this behaviour. It was found that in all cases, about 30% of the ionic monomers was incorporated into water soluble species, inducing high ionic strength in the dispersions. Very high ionic strength in the dispersions, difficultness to ensure complete protonation of the carboxylic acid groups in IA latex, and possible H-bonding between protonated COOH and the quaternary ammonium of DABCO might synergistically lead to instantaneous coagulation.

To avoid it, water-soluble polymeric (non-ionic) surfactants were employed as steric obstacle that eventually may postpone the ionic interactions, to have sufficient time to prepare the blend films before the blend dispersion was coagulated. Using Pluronic non-ionic surfactants, this idea was demonstrated in a recent work for blending of oppositely charged polymer particles in diluted dispersions (5 wt%) [19]. Pluronic family of surfactants are composed of triblock copolymers poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) (PEO-PPO-PEO), with different polymer brush length, which was the studied parameter. It was demonstrated that in very diluted polymer dispersions, when polymeric stabilizer with equal or higher chain length (L) than the Debye length (λ_D) of the particles was employed, overlapping of the double layers between adjacent particles is prevented, ensuring kinetically stable oppositely charged dispersions. It is also important to remark that when λ_D is equal or similar to L, the repulsion from the protective specie and the electrostatic attraction are balanced towards establishing of strong ionic bonds.

In this work, it was checked if this approach is valid in a case of highly concentrated dispersions (30% s.c.), in which maintaining sufficient distance between the oppositely charged particles is quite challenging. Moreover, different types of protective polymeric species were employed. Beside Pluronic-108, which was reported to have optimum

length for this aim [19], PVP and PVOH in different concentration and molar masses were used, too, based on previous good experience in waterborne composite systems stabilization, where often opposite charges in the different phases are present [22]. The polymeric stabilizers were added to the dialyzed charged polymer dispersions in a concentration range of 3%–40% based on total polymer (wbp%). As polymeric stabilizers can affect significantly the mechanical and water resistance of the polymer films, wide concentration range was studied in order to find the minimum necessary that will prevent particles coagulation after blending. The dispersion blends after addition of polymeric stabilizers were left under mild agitation to allow adsorption of the stabilizing units to the polymer particles, followed by blending of the stabilized oppositely charged dispersions, as illustrated in Fig. 3.

It is important to optimize the amount of the protective species, since their incorporation affects negatively the final properties of the material as poorer water and mechanical resistance [23–25]. In case when PVP and PVOH are used as stabilizers, they were not able to provide even short-term colloidal stability to the ionic blends. Even though both contain hydrophilic moieties pendant from the hydrophobic backbone, they did not have sufficient amphiphilic character as that of Pluronic F-108, provided by the three polymer blocks. The phase behaviour of this three block-co-polymer allows adsorption of hydrophobic PPG segment of Pluronic F-108 onto polymer particle surface, whereas the both PEG hydrophilic blocks are extended in water, forming denser shell around the particles. Pluronic F-108 in different concentrations (1–40 wbp%) was added in dialyzed latexes, which afterwards were mixed to create the blends (Blend C1-1 and Blend C1-1.8). In the case of Blend C1-1, 10 wbp% Pluronic F108 provided the most stable dispersion. The measurement of d_p after Pluronic F-108 addition in the blend did not show any change in the average particle size, demonstrating that the added stabilizers was adsorbed into particle surface and there was no Pluronic micelles formation in the dispersion.

Nevertheless, no stable blend dispersion was achieved for any of the studied concentrations in case of Blend C1-1.8, even at as high polymer concentration as 30 wbp%. The polymers addition increased the pH of the blend dispersion from acidic to neutral, which caused deprotonation of –COOH groups of IA containing particles. Taking into account the high charge density, this incited instantaneous coagulation.

The ionic interactions were studied for Blend C1-1 (IA1 – DABCO1), in which Pluronic F-108 was used to postpone the ionic bonding, leaving sufficient time to mix well the oppositely charged particles. After Pluronic F-108 addition, the pH of the polymer dispersions were changed from between 3 and 4 to 7, at which all functionalities were expected to be in their ionic form. Thus, no buffer was used to prepare the ionic complex material. To make a reference (a C1-1 blend without ionic complexation between the particles) phosphoric acid (sodium) buffer
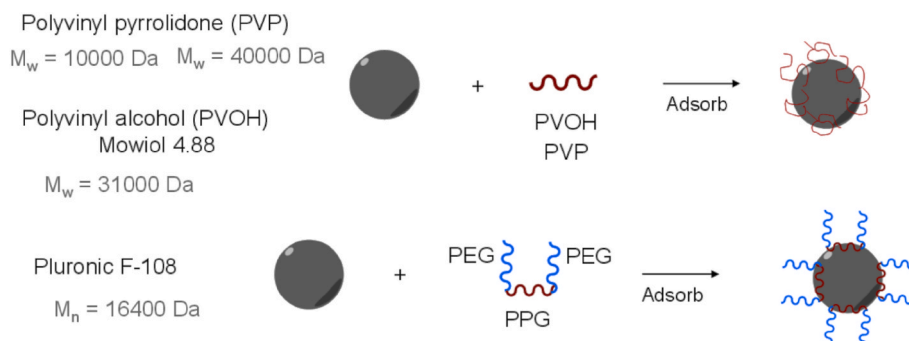
Fig. 3. Schematic representation of the adsorption of the polymeric/non-ionic stabilizers onto the polymer particles.

was used, which decreased the pH of the IA latex bellow pH < 3.8 to maintain the carboxylic functionalities protonated for preparation of the reference blend. The original polymer latexes synthesized using IA and DABCO functional monomers, and their blend dispersions obtained at different pHs (Blend C1-1, reference and ionic complex materials) were casted and dried. All of them gave rise to transparent films (Fig. 4), except the reference Blend C1-1 that presented lower transparency, indicating that the particles kept their borders within the film inducing light scattering. Probably the interdiffusion of polymer chains across the particles boundaries was suppressed due to formation of a thick ionomer phase with higher T_g, formed by the carboxylic acid groups (-COOH) and cations after neutralization at pH < 3.8, and therefore, providing resistance to diffusion across it [26].

The T_g of the Blends C1-1 (reference and ionic complex) and that of conventional MMA/BA are shown in Supporting information in Table S3. The T_g of conventional MMA/BA polymer was determined to be 17 °C, that of the reference blend was 18 °C, whereas the T_g of the ionic complex was 20 °C, which means that the T_g was not affected by the addition of the functional monomers neither by the ionic complexation process. This could be related to the low contribution of these functional monomers to the total formulation.

The surface morphology of the polymer films of Blend C1-1 (reference and ionic complex) was examined by AFM. Fig. 5 shows a representative AFM phase images of Blend C1-1, In Fig. 5a and 5c, where the reference blend film is shown, just one population of particles can be observed (light brawn aggregated particles), suggesting that particle segregation migh have occurred during the drying process. It has been reported previously that in a blended dispersion of neutral and charged particles, due to the difference in diffusion between charged and non-charged particles, segregation of the particles happen, leaving neutral particles on the film surface and the charged ones within the film away from the air-film interface [27]. Taking into account that in our work the reference blend is a mixture of neutral and cationic particles, it is likely that the particles that we observed in Fig. 5a and 5c are the neutralized IA particles. However, in Fig. 5b and 5d, where the ionic complex material is presented, a more homogeneous structure can be appreciated, made of the light brown individual particles, each surrounded by dark brown material. We attributed the lack of aggregates made of single particle population to formation of ionic complexes between the oppositely charged particles.

To determine the mechanical resistance of the films, tensile tests were performed. The tensile properties of the films are shown in Fig. 6 and Table 3, where the reference and ionic complex blends were compared to the original IA1 and DABCO1 individual polymer films.

Fig. 4. Appearance of the individual polymers (IA1 and DABCO1) and the blend C1-1 films at different pH's (reference and ionic complex).
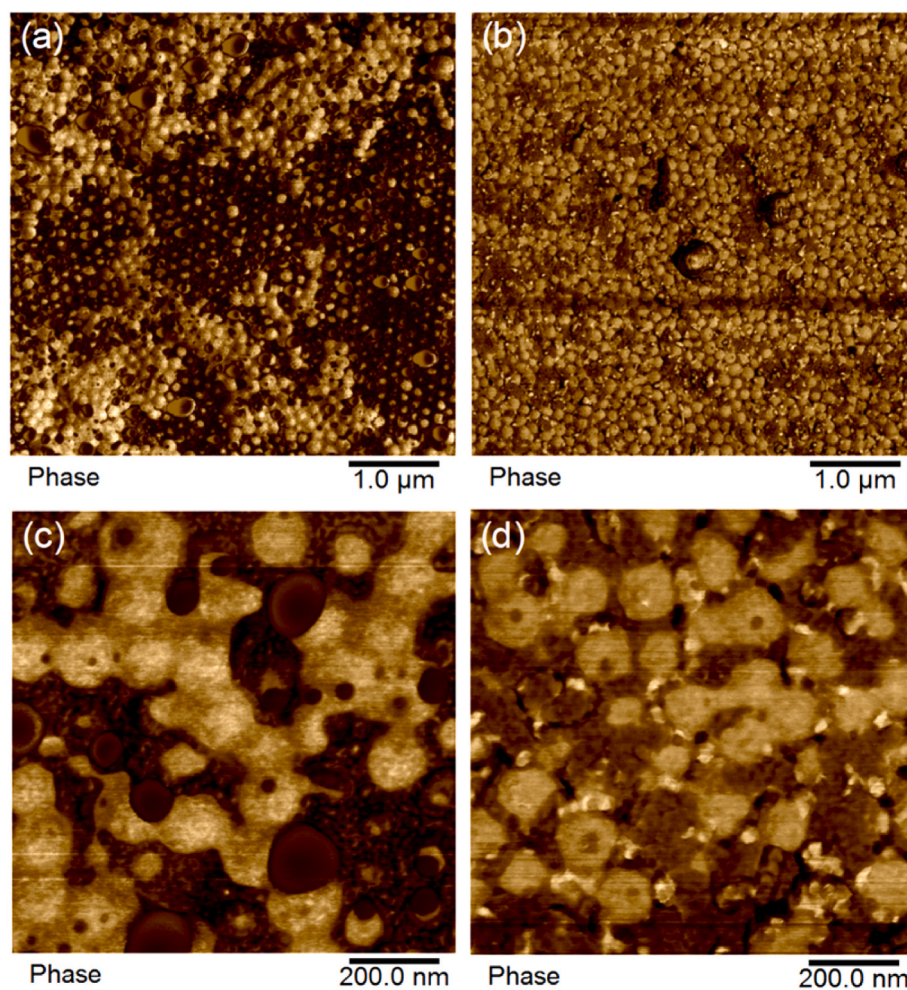
Fig. 5. AFM air-film interface phase images for Blend C1-1 at 5 and 1 μm scale and at different pH's. (a) and (c) refers to the reference material, while (b) and (d) refers to the ionic complex one.
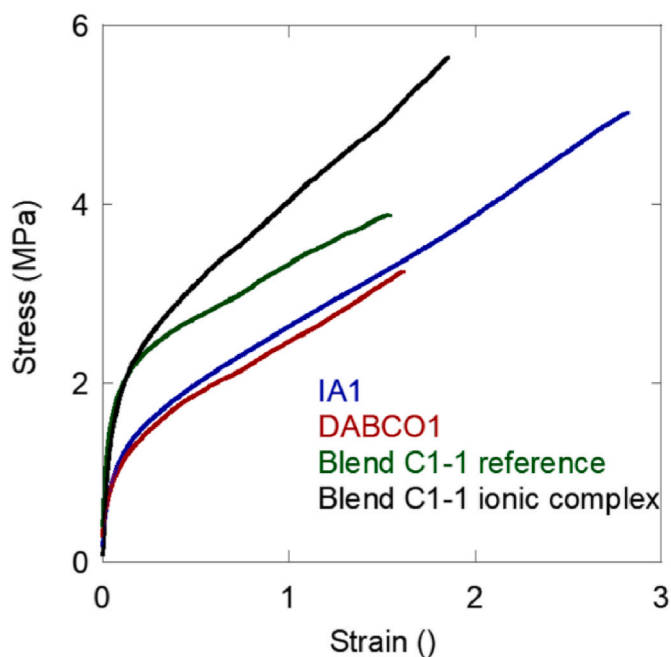

Fig. 6. Mechanical properties of individual polymer films (IA and DABCO) and their blends (Blend C1-1, reference and ionic complex).

Table 3
Parameters of the original polymer films and Blend C1-1 films related to the stress-strain plots represented in Fig. 6.

Sample		Young modulus (MPa)	Elongation at break	Ultimate strength (MPa)	Toughness (MPa)
IA1		13 ± 2	2.8 ± 0.6	5.1 ± 0.1	8.7 ± 1.1
DABCO1		16 ± 1	1.5 ± 0.6	3.3 ± 0.6	3.5 ± 0.6
Blend	Reference	30 ± 3	1.3 ± 0.2	3.3 ± 0.4	3.4 ± 0.9
C1-1	Ionic complex	28 ± 2	2.0 ± 0.1	5.9 ± 0.4	7.9 ± 0.9

Pluronic F-108 was added as well to the original latexes in the same quantity to mask the effect of this stabilizer in the tensile behaviour.

As it can be seen in Fig. 6, DABCO1 film showed slightly higher Young modulus than IA1 film, as DABCO units added rigidity to the chains due to the cyclic structure. Nonetheless, higher elongation at break, ultimate strength and toughness values were obtained for the film containing IA, which could be attributed to the dimerization of carboxylic acid moieties present in the polymer chains, as reported previously [28].

Regarding the Blend C1-1 films, an increase in the Young modulus was observed for both, the reference and the ionic complex materials from about 13 to 16 MPa of the individual films up to 28–30 MPa for both blends reference and complexed. Considering the lack of ionic complexation in the reference blend, this result is rather surprising.

Likely, this enhancement can be related to the mentioned effect of carboxylic acid dimers formation, promoted by the fact that most of the carboxylic acids groups at the pH of 3.5 at which the reference was prepared are in their protonated form. Moreover, due to the high charge density, probably the ionic complexation could not be completely prevented. In the case of the C1-1 ionic complex, the mechanical properties are further improved with respect to both individual films (IA1 and DABCO1) and the reference blend. While both blends present similar elastic moduli, the ionic complexed film presents higher ultimate strength (5.9 MPa vs. 3.3 MPa for the reference) and toughness (7.9 MPa vs 3.4 MPa of the reference). Even though the stiffness of the ionic complexed film was doubled than that of the individual films, the film presents significant elongation at break, which was attributed to the dense ionic complexed network established between the polymer particles when the film was formed. A scheme of these physical interactions presented within the blends are shown in Fig. 7.

It is worth mentioning that the observed improvement of the mechanical properties due to doubled charged monomers is much more important than in our recently reported work, in which functional monomers containing one ion per molecule were used for the same aim [11]. This result is a clear indication of the effect of a denser ionic network due to the ionic monomers containing two charges per molecules on the performance of the complexed film.

Most of the waterborne coating films contain ionic groups coming from surfactants or additional functionalization [16], the presence of which impact the coating's water sensitivity [8,16]. To determine how the ionic bonding affect the water sensitivity of Blends C1-1 reference and ionic complex, water uptake of the films was studied by their immersion in water for 14 days. Fig. 8a shows the film weight evolution upon water absorption during 14 days.

As observed, the individual IA1 and DABCO1 films showed high water uptake (10 wt% and 8 wt%, respectively) during the first hours of immersion due to the presence of soluble polymer chains rich in ionic functionalities, but as well the Pluronic surfactant added before the film formation. It is worth mentioning that even so, these values are importantly lower than the water uptake of BA/MMA films, stabilized with conventional surfactant, usually higher than 15 wt% [8,16]. This is likely due to chemical incorporation of the functional monomer IA and DABCO onto BA/MMA particles, which prevent migration of stabilizing units and formation of hydrophilic pockets that rise the water sensitivity in case of conventional surfactants for instance Ref. [16]. The water adsorption is relatively fast and finished approximately in 2 h, after which the individual film lost weight, likely due to solubilisation of all water-soluble species, including Pluronic F-108 and their diffusion in the water. After the initial adsorption/desorption processes, the weight of the films remains constant, with exception of DABCO1 individual film that continue losing weight until all added quantity of Pluronic-F-108 was extracted from the film, likely because only within DABCO

containing film, there is no interaction of Pluronic F-108. Namely, in the case of IA containing film Pluronic might be strongly bonded by building a H-bridge interactions with the carboxylic acid functionalities. This behaviour can be appreciated in Fig. 8b, which illustrates a zoomed area of the initial water uptake period (two days).

On the other hand, both Blend C1-1 films reference and ionic complex absorbed even lower water quantity (7 and 6 wt%, respectively) than the individual films, likely due to the lower quantity of ionic species in case of the reference blend and due to the neutralization of the free ionic species during the ionic complexation. Surprisingly, the desorption of the water-soluble polymeric species present within the blends is as well lower than from the individual films, being the lowest from the ionic complexed film (0.8 wt%). While the reference blend that contain free IA functionalities retained some of the Pluronic species by the H-bonding, the ionic complexed blend captured completely these water soluble polymer chains. The last effect is caused likely by the strong ionic network established within the film that prevented their leaching from the film. This evidence can be very useful for preventing the leaching of surfactants from waterborne films into environment or for introducing barrier capability within the MMA/BA – based coatings.

This behaviour was further demonstrated by measuring the weight loss of the material after water immersion. Films were dried and weighted before and after the immersion in water in order to determine the weight loss of the materials. The weight loss (wt%) is referred to the initial weight of the films and the results are presented in Fig. 9.

As it can be seen, the films containing the functional monomers IA and DABCO (IA1 and DABCO1 films) and the Blend C1-1 reference materials lost more weight than the Blend C1-1 ionic complex probably owed to the physical obstacles formed as already mentioned.

4. Conclusions

In attempts to overcome the main challenge of the waterborne polymer coatings films of lower performance induced by the particulate nature of the polymer dispersions and the complex process of film formation, in this work we implemented the strategy of ionic complexation between oppositely charged MMA/BA waterborne particles. For that aim and for first time to the best of the authors' knowledge, doubled charged ionic monomers were selected in order to decrease the needed quantity of ionic monomer and simultaneously to increase the ionic charge density. IA and DABCO ionic monomers were copolymerized with MMA/BA main monomers by seeded semibatch emulsion polymerization to produce anionically and cationically charged particles, respectively.

The blending process of these densely charged and highly concentrated polymer dispersions has shown to be challenging process due to immediate coagulation, which could not be controlled by the pH of the dispersions and the ionic state of the ionic functional groups. This
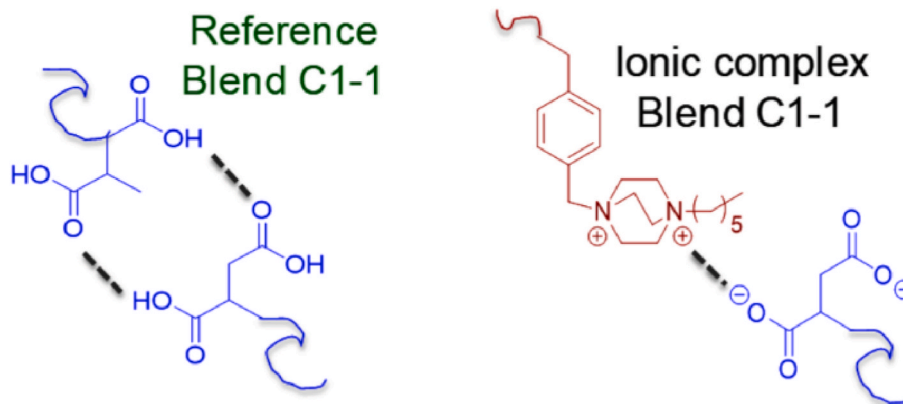

Fig. 7. Scheme of the physical interaction in Blend C1-1, reference and ionic complex.
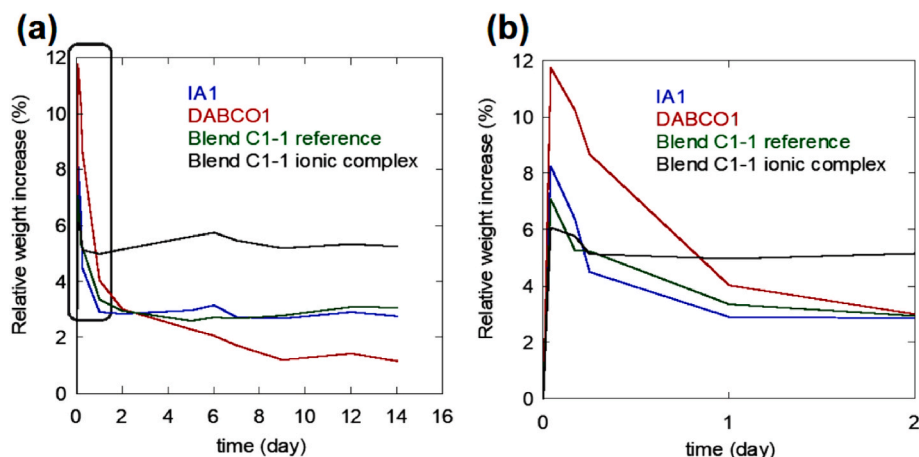
Fig. 8. Water uptake of original polymer films (IA1 and DABCO1) and their blends (C1-1, reference and ionic complex) during (a) 14 days of water immersion and (b) zoomed area of the initial water uptake period (2 days).
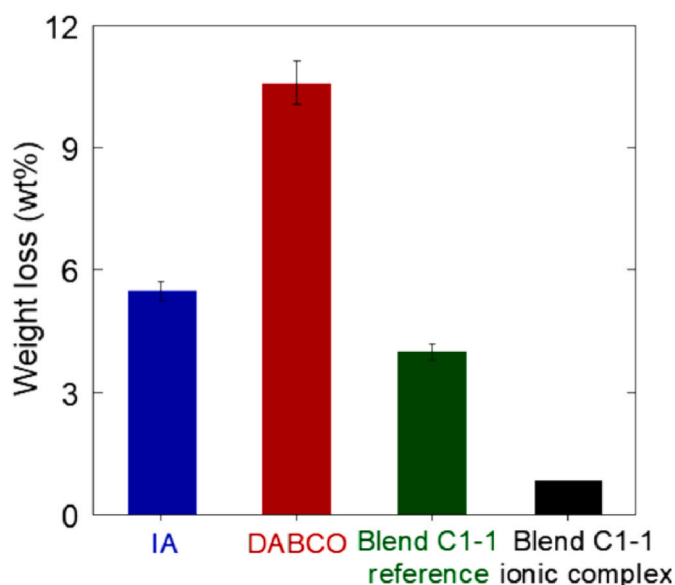

Fig. 9. Weight loss (wt%) values after water uptake experiments for original films (IA and DABCO) and polymer blend films (reference and ionic complex).

challenge was resolved by a use of Pluronic F-108 non-ionic surfactant that after the addition to the dispersions in 10% wt quantity, postponed the ionic complexation and enabled the blends and their films preparation. Reference blend, in which the ionic complexation was avoid, was prepared at pH < 3.8, where IA species are in their molecular state.

Mechanical properties of both blends reference and ionic complexed were improved with respect to both individual polymer films (IA and DABCO containing), being the ionic complexed film with the best mechanical resistance. The reference film improved stiffness was attributed to the dimerization of carboxylic acid moieties from IA units and the difficultness to prevent the ionic complexation in such densely charged dispersions. In the case of the C1-1 ionic complex, the mechanical properties were further improved with respect to both individual films (IA and DABCO) and the reference blend due to the formation of strong ionic complexes. The effect of the ionic complexation was also observed in the water uptake test, where ionic complex material presented very low water adsorption (less than 6%). The ionic complexed blend prevented Pluronic F-108 polymeric stabilizer leaching from the film to the water phase, while this encapsulation effect of polymeric stabilizer was not observed in IA1, DABCO1 and the reference blend films, which

presented more important water adsorption and afterwards loss of weight due to leaching of water soluble species from the film to water.

The presented inter-particle complex between deprotonated carboxylic groups of IA and quaternary ammonium units from DABCO containing latexes open an interesting route for reinforcing MMA/BA polymer films cast from water-based polymer dispersion, but as well widen their application possibility towards barrier coatings.

CRediT authorship contribution statement

Maialen Argaiz: Formal analysis, Investigation, Resources, Data curation, Writing – original draft. **Miren Aguirre:** Methodology, Validation, Supervision, Writing – review & editing, Visualization. **Radmila Tomovska:** Conceptualization, Methodology, Supervision, Writing – review & editing, Project administration.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2022.125571.

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