



## Self-matting waterborne fluoropolymers

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### ABSTRACT

This work describes a study on the incorporation of waterborne fluoropolymer dispersions into paint formulations to act as a film forming binder for matting purposes. The waterborne fluoropolymer dispersions were prepared employing miniemulsion polymerization, reaching concentrations of 80–100 wt% of the fluorinated polymer in the backbone. Afterwards, different pigmented paints were prepared using the waterborne fluoropolymers as self-matting co-binders. Different strategies were used to incorporate the waterborne fluoropolymers into the paint formulation, which also included the partial substitution of commercial matting agents. The pigmented paints were applied onto different substrates and the matting efficiency evaluated. The results clearly showed that these waterborne fluoropolymers can be used as an alternative replacement for commercial matting agents, while adding value to the coating by offering enhanced hydrophobicity as compared to regular acrylic binders.

### 1. Introduction

Emulsion polymers have shown to be an excellent alternative to their counterpart solventborne polymers when used as binders for coatings and adhesives [1,2]. The reduced emission of volatile organic compounds provided by waterborne (WB) polymers is amongst others the primary for reason for their selection when formulating paints or coatings for architectural, decorative or industrial wood purposes [3,4]. Recent data shows that around 80% of paint sold in the residential market is water-based [5].

Waterborne acrylic dispersions have been widely used as binder in different coatings applications. The durability of the paints or coatings formulated with these binders depends on their resistance to several factors such as: UV-light, exposure to water, seasonal temperature changes and microbial attack. Waterborne binders can be especially sensitive to water due to the presence of surfactants during their preparation and/or the hydrophilicity of some acrylic polymer in the particles. As a consequence the paint/coating could suffer from poor water resistance, blistering, and delamination particularly in outdoor applications in which the water accumulates. In that sense the incorporation of hydrophobic components into the formulation as well as the use of hydrophobic polymer binders such as long chain methacrylates and styrene is an efficient way to improve water resistance of paints [6].

Among the different hydrophobic binders, fluorinated polymers are well known to have excellent water repellency. Moreover, fluorinated polymers can greatly enhance the properties of coatings used in modern industrial, household and construction products. These materials combine a wide variety of interesting properties that are beneficial for coating formulations such as low surface energy, insulating properties, impermeability to gases, high resistance to water, oil, chemicals, corrosion and UV- radiation as well as low dirt pick up [7–13]. Indeed, many fluorinated polymers (e.g. polytetrafluoroethylene (PTFE, Teflon), polyvinylfluoride (PVF), polyvinylidene fluoride (PVDF) or fluoroethylene vinyl ether (FEVE)) are already being used in the market as a part of industrial settings, insulation systems and food and automotive industry [14].

Fluorinated monomers are highly insoluble in water, which represents an essential drawback when preparing waterborne dispersions using emulsion polymerization. In emulsion polymerization, monomer transfer to the polymerization loci is needed<sup>1</sup> and the transport by collision is not fast enough [15]. Different attempts can be found in the open literature [16–18] or industrial patents [19–21] to produce waterborne fluoropolymer through emulsion polymerization. In most of the cases [16,19–21] the main monomers are vinylidene fluoride, hexafluoropropylene, and tetrafluoroethylene which required the use of complex pressurized reactors. In other cases acrylic core-shell like particles were prepared by using 12–30 wt% (based on total monomers

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**Table 1**  
Formulation of the fluorinated homopolymer and copolymers.

Organic phase		Aqueous phase		$d_{\text{droplet}}$ (nm)	$d_{\text{particle}}$ (nm)
Monomer ratio <sup>a</sup> (wt/wt/wt)	Initiator <sup>b</sup>	Emulsifier <sup>b</sup>	Water		
PFDA/2EHA/MAA (100/0/0)	AMBN	DOWFAX 2A-1	≈ 60 wt%	154	228
C100	1 wt%	1 wt%			
PFDA/2EHA/MAA (88.6/9.9/1.5)	AMBN	DOWFAX 2A-1		150	236
C88	1 wt%	1 wt%			
PFDA/2EHA/MAA (80.8/17.7/1.5)	AMBN	DOWFAX 2A-1		156	240
C80	1 wt%	1 wt%			

<sup>a</sup> Monomer represents 40% of the total weight of the formulation.

<sup>b</sup> Based on the total weight of monomer.

weight) of dodecafluoroheptylmethacrylate. Even though the hydrophobic character of the films was described, no results on the monomer conversion were presented, as post-treatment was needed to remove residual monomers [17,18]. Miniemulsion polymerization has shown to be a well suited technique to prepare waterborne polymers with highly hydrophobic monomers since the transport through the aqueous phase is not needed as the main loci of reaction are the preformed monomer droplets [22–24]. Fluorinated monomers have been previously polymerized in aqueous media by miniemulsion polymerization. Landfester et al. [25] obtained contact angles around 130° when the film was formed at 50 °C, at room temperature the contact angles reached 105°. When a fluorinated reactive surfactant was employed for stabilizing acrylic particles the contact angle only reached 85° [26]. Recently it has been demonstrated by López et al. [27,28], that is possible to copolymerize monomers such as 1H,1H,2H,2H-Perfluorodecyl acrylate (PFDA) and 2-ethyl hexyl acrylate (2EHA) using miniemulsion polymerization in a batch process. Different stable dispersions were produced that once film-formed, presented a controlled topography that allowed obtaining contact angles higher than 130°.

Nowadays, there is a continuous and increasing trend in using functional coatings for matte surfaces. There are many applications in which the glossy aspect is not desired [29]. For instance, in the furniture industry it is demanded to bring out the natural structure of the wood (a coated piece that looks naturally uncoated) [30]. In addition, high-gloss coatings often show to the naked eye grease contamination and fingerprints, which is not the case for the natural look of matte coatings [31,32]. There is a quite large offer of matting agents that can be used in waterborne paint/coatings formulations. In most of the cases, these agents are based on treated silica, polyethylene waxes and/or micronized organic polymers amongst others. The compatibility of the matting agents and their incorporation into the paint formulation with the waterborne binder is complex and it often requires different and large pre-screening analysis to make a further selection. Moreover, the matting agents in most of the cases do not offer extra properties to the films. In that sense it would be ideal to have a matting agent that has the similar nature of a waterborne acrylic binder. Nunes et al. [33] employed waterborne acrylic nanoparticles as additive to enhance the fat resistance of pigmented waterborne topcoats. Waterborne fluropolymers have been developed to be used in paints/coatings as a binder to improve the weatherability performance [34,35]. On the other hand, there are examples in which waterborne polyurethanes were used as binders for self-matting coatings [36,37]. To the best of our knowledge, no previous study has shown the use of waterborne fluropolymers with a dual function of film-forming binder and self-matting characteristic.

In the present work, fluorinated homopolymer and copolymer latexes using PFDA as fluorinated monomer, 2-ethylhexyl acrylate (2EHA) as comonomer to improve film formation properties and methacrylic acid (MAA) were synthesized and incorporated into a commercial paint formulation. Initially, the study will be focused on the aspects related to the preparation of the waterborne fluorinated

binders. Afterwards, the effect of the incorporation of such dispersions in pigmented coatings with regards to the matting efficiency and the hydrophobicity will be described.

## 2. Materials and methods

1H, 1H, 2H, 2H-perfluorodecyl acrylate (PFDA, supplied by Interchim), 2-ethylhexyl acrylate (2EHA) and methacrylic acid (MAA) (supplied by Repsol Química S.A.) were used as monomers. Dowfax 2A1 (alkyl diphenyloxide disulfonate from Dow Chemical) was used as surfactant. 2,2'-Azodi(2-methylbutyronitrile) (AMBN, supplied by Akzo Nobel) was used as oil soluble initiator.

### 2.1. Synthesis of waterborne fluorinated resins

The miniemulsification process is still the bottleneck for the industrial implementation of miniemulsion polymerization. High pressure homogenizers (HPHs) seem to be a promising choice for industrial scale as large capacity HPHs are available [24]. In this equipment, the size and the broadness of the droplet size distribution decrease with the number of passes or homogenization cycles, therefore, several passes are often needed to achieve small droplet sizes [38,39]. A high pressure homogenizer APV-1000 was used in this work to prepare the mini-emulsions. This equipment has two valves operating at  $P_{\text{max}} \approx 80$  MPa and  $P_{\text{min}} \approx 12$  MPa respectively.

Different polymer binders were synthesized as it is represented in Table 1. For the preparation of the miniemulsions, the organic phase (monomer and initiator) and the aqueous phase (emulsifier and water) were mixed separately for 15 min and then, they were mixed together for another 15 min obtaining a coarse emulsion. This emulsion was charged to the homogenizer for the miniemulsification process. Several cycles were necessary to achieve a target droplet size of around 150 nm and a good miniemulsion stability. Fig. 1 represents the evolution of the droplet size with the number of cycles of homogenization for the three different compositions.

After the homogenization stage, the miniemulsions were charged

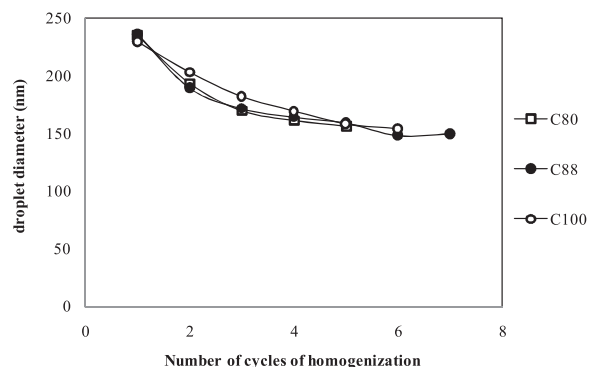


Fig. 1. Evolution of droplet size with the number of homogenization cycles.

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