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Production of colloidally stable latices from low molecular weight ethylene–propylene–diene copolymers

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Abstract

The best impact modifiers for coatings and engineering plastics include fixed morphology core-shell particles. For the present work, ethylene–propylene copolymers (EPM) and ethylene–propylene–diene copolymers (EPDM) were chosen, for their good resistance to stringent conditions, like UV-irradiation or high temperatures, to prepare the core of the desired particles.

The solution-emulsification technique was used to produce artificial latices based on low molecular weight EPM and EPDM materials. Conventional emulsification techniques as well as 'miniemulsification' methods have been investigated. In both cases, a larger volume of polymer is reduced into smaller sub-units using the mechanical energy of comminution techniques, i.e. an Ultra-Turrax® and a homogenizer operating at a pressure of 300 bar and with a shear rate of approximately $3.2 \times 10^7 \, s^{-1}$. The difference between conventional emulsification and miniemulsification resides in the stabilizing system. For the conventional emulsification method, an equimolar mixture of anionic (sodium dodecyl benzene sulfonate, SDBS) and nonionic (polyoxyethylene (100) stearyl ether, Brij 700) surfactants was found to be the optimal surfactant system. For the miniemulsification method, a combination of SDBS as surfactant and hexadecane or cetyl alcohol as costabilizer was the most suitable system. Both conventional emulsification and miniemulsification lead to latices with monomodal particle size distributions and volume-average diameters ranging from 300 to 400 nm, determined with light scattering techniques. The low molecular weight elastomers, exhibiting viscosities lower than 1 Pa s at 20 °C, were easily emulsified without addition of organic solvent.
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1. Introduction

Increasing environmental concerns in the formulations of various coating compositions such as paints or adhesives has generated considerable interest in producing a wide variety of synthetic organic polymers in a latex form. The preparation of vinylic polymer latices by emulsion polymerization techniques is well known. Typical products include polybutadiene, polystyrene, poly(styrene-acrylonitrile), and poly(methyl methacrylate) latices.

However, synthetic limitations, such as the need of water-sensitive catalysts, prevent the production of many polymers in aqueous dispersions. This is the case, for instance, for polyolefins such as polyethylene, polypropylene, and ethylene–propylene copolymers (EPM), as well as copolymers of one or more olefins with other monomers (e.g. non-conjugated dienes). An example of the latter is ethylene–propylene–diene monomer (EPDM), which is the preferred elastomer for application as impact modifier for coatings and engineering plastics.

A dispersion of EPDM-based polymers in water is obtained through the preparation of an artificial latex, i.e. a preformed polymer colloidally dispersed in an aqueous medium [1]. Among all the processes developed for the production of artificial latices, two techniques are mostly used: the phase-inversion technique and the solution-emulsification technique. The phase-inversion technique [2] has been employed by Yang et al. [3] to prepare waterborne dispersions of epoxy resin. By dispersing, under stirring, increasing amounts of water into the emulsifier (or surface-active agent) containing polymer, at a temperature ranging from 60 to 80 °C, a water-in-oil dispersion is initially formed. As more aqueous phase is incorporated, a phase inversion occurrence becomes increasingly likely,

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thereby creating the desired dispersion of the polymer in an aqueous medium. However, depending on the emulsifier concentration and on the temperature, a complex water-in-oil-in-water structure can be achieved by incomplete phase inversion. Therefore, a better controlled technique, i.e. the direct solution-emulsification technique, reported by Burton and O'Farrell [4], can be used. It consists of the dissolution of the polymer in a volatile solvent to form a solution or cement. The resulting solution or cement is then emulsified in water with one or more emulsifiers to form a crude emulsion. The 'droplet' size in the crude emulsion is then reduced to submicron size by application of a high shear rate (namely the homogenizing step). The final step of the procedure is the removal of the solvent from the emulsion, by reduced pressure or steam distillation.

When producing artificial latices, numerous parameters have to be taken into account. One of them is the emulsifier, which is critical for the formation of an emulsion that should remain stable at the relatively high temperature and under the mechanical forces of both the homogenizing step and the stripping operation.

The colloidal particles are permanently subjected to the influence of the van der Waals–London attractive forces. Hence, in order to maintain colloidal stability and outweigh those attractive forces, an electrostatic and/or steric repulsion has to be introduced. Various types of surfactants have been employed for the synthesis and stabilization of polymer latices [5]. Electrostatic stability is provided by ionic surfactants as described in the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [6,7]. The coverage of the particles by charged species creates an electric double layer, leading to electrostatic repulsion. Steric stabilization [8–10] is obtained with nonionic or polymeric surfactants in many cases based on polyethylene oxide as the hydrophilic part. The robustness of the steric stabilization method can be exemplified by its relative insensitivity to high concentrations of electrolytes and its tolerance to temperature effects such as freeze-thawing [11]. Note that, for nonionic surfactants, the critical coagulation temperature should not be exceeded. The combination of both stabilization mechanisms, by using anionic and nonionic surfactants, offers remarkable results. Colombié et al. [12] used for instance a mixture of sodium lauryl sulfate and Triton X-405 (octylphenoxy poly(ethylene oxide)) to stabilize submicron polystyrene particles dispersed in water. Another approach relies on the use of electrosteric surfactants, which consist of an ionic charge chemically bonded to the end of the hydrophilic nonionic moiety. An example of a surfactant providing both electrostatic and steric stabilization is the commercially available series Avanel S, $C_mH_{2m+1}O(CH_2CH_2O)_nSO_3Na$ (with $12 \leq m \leq 15$ and $3 \leq n \leq 15$) (PPG Industries) used by Sung and Piirma [13] in the emulsion polymerization of styrene.

The term miniemulsion describes a submicron oil-in-water dispersion with colloidal stability ranging from hours to months [14]. A practical application of the procedure to produce miniemulsions, i.e. miniemulsification[1], is found in the preparation of artificial latices from polymer solutions, as reported by El-Aasser [15]. Indeed, the miniemulsification method may be employed for the emulsification of non water-miscible polymer solutions in aqueous media containing the proper emulsifier system. After emulsification, the solvent can be removed by steam distillation under vacuum. However, as opposed to a conventional emulsion, a miniemulsion is stabilized by a combination of an efficient ionic surfactant and a costabilizer, i.e. a highly water-insoluble low-molecular weight compound. This approach to emulsion stability issues was first reported by Higushi and Misra [16]. The main reason for the destabilization of an emulsion is related to chemical potential differences. Indeed, the chemical potential of the monomer in small droplets is higher than that in large droplets or plane surfaces. Consequently, monomer diffuses from small to large droplets leading to larger droplets and partial emulsion degradation. This phenomenon is referred to as Ostwald ripening. Higushi and Misra [16] considered that both the rate of growth of large particles and the rate of dissolution of small particles were diffusion controlled. Therefore, the addition of a small amount of a water-insoluble compound would retard the emulsion degradation due to its slow diffusion rate, and the monomer distribution over the particles would not change during a long elapse of time. Typical costabilizers include long chain alkanes and fatty alcohols, more specifically hexadecane and cetyl alcohol. For example, Hansen and Ugelstad [17] used styrene as monomer and hexadecane as costabilizer, while Rodriguez [18] used styrene and methyl methacrylate with both hexadecane and cetyl alcohol.

Finally, the viscosity of the dispersed phase represents another key parameter for the emulsification of a polymer. According to Burton and O'Farrell [4], the cement must exhibit a viscosity lower than 10 Pa s at 24 °C to be properly dispersed, leading to particles with an average diameter below one micrometer. The viscosity of the cement is of course dependent on the molecular weight and molecular structure of the polymer, as well as on the polymer concentration in the solution.

The direct solution-emulsification technique has been extensively used [19–22] to produce high molecular weight ethylene–propylene–diene copolymers in a latex form. Number-average molecular weights of the polymers ranged from 75×10^3 to 200×10^3 g mol^{-1} and their viscosities were higher than 10 Pa s at room temperature. Therefore, in order to obtain low viscosity cements, the polymers had to be diluted with non water-miscible solvents, the organic phase containing up to 25 wt% solid, preferably about

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[1] The term miniemulsification does not exist as such in the miniemulsion terminology. However in the remainder of this paper, it will refer, as suggested by El-Aasser et al. [15], to the process of dispersing a polymer in water, stabilized by a combination of an anionic surfactant and a costabilizer.

Table 1
Description of the surfactants

Name	Description	Structure	Supplier	HLB[a] Value	M_n (g mol^{-1})
SDBS	Sodium dodecyl benzene sulfonate	$CH_3\!-\!(CH_2)_{10}CH_2\!-\!\bigcirc\!-\!S(=O)(=O)\!-\!ONa$	Fluka	11.7	348.5
Brij 97	Polyoxyethylene (10) oleyl ether	$C_{18}H_{35}\!-\!(O\!-\!CH_2\!-\!CH_2)_{10}OH$	Aldrich	12.4	709
Igepal CO-890	Polyoxyethylene (40) nonylphenyl ether	$C_9H_{19}\!-\!\bigcirc\!-\!(O\!-\!CH_2\!-\!CH_2)_{40}OH$	Aldrich	17.8	1982
Brij 700	Polyoxyethylene (100) stearyl ether	$C_{18}H_{37}\!-\!(O\!-\!CH_2\!-\!CH_2)_{100}OH$	Aldrich	18.8	4670

[a] HLB = Hydrophilic–lipophilic balance.

5–20 wt% solid. As a consequence, in order to minimize the amount of solvent that has to be removed, polymer concentrations have to be brought to their maximum within the limits set for proper emulsification.

The solvent (or the solvent/water azeotrope) must exhibit a boiling point lower than the boiling point of water. Thus, solvents of choice include aromatic hydrocarbons (e.g. toluene), but also aliphatic hydrocarbons (e.g. pentane, heptane).

However, for environmental, economic, and time-saving reasons, a step forward would be made with the preparation of solventfree artificial polymer latices. Thus, the aim of the present work is to develop a procedure for the production of such latices with submicron EP(D)M particles. The choice of EP(D)M is particularly relevant for its use in environments where weatherability is an important property. Indeed, as a saturated-main chain rubber, it exhibits good stability not only towards oxygen and UV irradiation, but also towards hydrolysis and high temperatures. The submicron size of the particles is a prerequisite for the formation of core-shell structures, used as impact modifiers for coatings and engineering plastics. The artificial EP(D)M latex is the starting material for crosslinking and grafting reactions leading to core-shell structures. Crosslinking of the EP(D)M core will preserve its spherical shape upon injection molding. Grafting of methyl methacrylate by seeded emulsion polymerization onto the rubber core will generate a glassy shell, compatible with targeted polymer matrices.

Moreover, a glassy PMMA shell will provide a free-flowing character to the impact modifier.

In this paper, the emulsification process will be discussed in terms of conventional and miniemulsification processes. The choice of the surfactant system for an optimal stability of the produced EP(D)M-based latices will be emphasized. Finally, the influence of the cement viscosity on the emulsification process will be discussed.

2. Experimental section

2.1. Chemicals

Surfactants, n-heptane (Biosolve), hexadecane (Aldrich), and cetyl alcohol (Aldrich) were used as received. Deionized water was used for all latices. The structures and characteristics of the polymers and surfactants used in this study are summarized in Tables 1 and 2.

2.2. Characterization of polymers

2.2.1. Molecular weights

Number- and weight-average molecular weights (M_n and M_w) as well as molecular weight distributions were determined using a Waters 2690 Alliance Size Exclusion Chromatograph (SEC) equipped with two Styragel HR 5E columns, a Waters 410 differential refractometer, and a Viscotek T50A differential viscosimeter. The eluent was

Table 2
Properties of the polymers studied

Polymer number	Polymer name	Supplier	Type of diene	M_w (g mol^{-1})	Ethylene content (mol%)	Propylene content (mol%)	Diene content (mol%)
P1	Lucant® HC-20 (EPM)	Mitsui Chemicals, Inc.	–	1450	58	42	–
P2	EPM 01371L	DSM Elastomers	–	8690	66	34	–
P3	EPDM 99488K	DSM Elastomers	Ethylidene norbornene	12,679	70	28	2
P4	EPDM 99488L	DSM Elastomers	Ethylidene norbornene	21,397	74.7	22.7	2.6
P5	Trilene 67 (EPDM)	Crompton Corp.	Ethylidene norbornene	28,716	65	32.6	2.4

Table 3
Recipes for conventional emulsifications

Emulsification number	Polymer			Heptane (g)	Water (g)	Surfactants[a]	
	Type	Amount (g)	Weight fraction in the latex (%)			Type	Amount (g)
E1	Lucant® HC-20 (EPM)	30.9	23.4	–	100.1	SDBS	0.9
E2	Lucant® HC-20 (EPM)	30.4	23.0	–	100.1	Brij 97	1.8
E3	Lucant® HC-20 (EPM)	30.1	22.2	–	100.1	Igepal CO-890	5.0
E4	Lucant® HC-20 (EPM)	30.1	21.2	–	100.0	Brij 700	12.1
E5	Lucant® HC-20 (EPM)	30.2	22.8	–	100.0	SDBS + Brij 700 (90–10)	0.8 + 1.2
E6	Lucant® HC-20 (EPM)	30.2	22.1	–	100.1	SDBS + Brij 700 (50–50)	0.4 + 6.0
E7	Lucant® HC-20	30.0	22.8	–	100.1	SDBS + Brij 97 (50–50)	0.5 + 0.9
E8	Lucant® HC-20 + EPDM 99488K	30.2 + 10.0	20.9	10.1[b]	135.2	SDBS + Brij 700 (50–50)	0.4 + 6.2

[a] In all cases: (Emulsifier/$EP(D)M$) $\times$ 100 $\approx$ 12.2 mol% and the total concentration of emulsifier in water is 2.6×10^{-2} mol dm^{-3}.

[b] Weight fraction of organic phase in the latex: 26.1 wt%. The calculations are based on M_w of each polymer, given in Table 2.

THF, and the elution volumetric flow rate was maintained at 1 ml min^{-1}. Absolute molecular weights were calculated by performing universal calibration using polystyrene standards.

2.2.2. Composition

Copolymers compositions were determined by ^{1}H and ^{13}C nuclear magnetic resonance (NMR), on a Varian-500 spectrometer at 25 °C, using TMS as internal standard and CDCl$_3$ as solvent.

2.2.3. Viscosities

All viscosities (Pa s) of pure polymers and polymer/n-heptane mixtures were measured at 20 °C as a function of the shear rate (s^{-1}) with an AR 1000-N rheometer from TA Instruments.

2.3. Characterization of latices—particle size distribution

Particle size distributions and volume-average diameters of the latex particles were determined with a Coulter LS 230. This analyzer uses the principles of light scattering, based on both Fraunhofer and Mie theories, to determine particle size distributions. Moreover, the range of detectable particle sizes is extended to the submicron region (lower size limit: 40 nm of diameter).

2.4. Preparation of an artificial latex from a low molecular weight EP(D)M

2.4.1. Conventional emulsification

Recipes are collected in Table 3. If necessary, the first step involved the dissolution of the polymer in *n*-heptane in order to reduce its viscosity. Surfactant was separately dissolved in water with a similar molar concentration of surfactant for all the systems studied. In a second step, the organic phase was brought into the aqueous phase, the resulting blend being stirred for 1 min with a rotor-stator Ultra-Turrax® T25 Basic at 24,000 rpm. The size of the eventually swollen polymer particles was reduced by processing the emulsion product of the Ultra-Turrax® in a Niro-Soavi Lab homogenizer NS1001L Panda operating at 300 bar, with a shear rate of approximately 3.2×10^7 s^{-1}. Processing times ranged from 1 to 3 h, depending on the viscosity of the samples.

2.4.2. Miniemulsification

Recipes are collected in Table 4. Both hexadecane and cetyl alcohol were employed as costabilizers to produce artificial latices. When hexadecane was used, it was mixed with the organic phase before addition to the aqueous phase. However, as stated by Brouwer et al. [23], the initial presence of cetyl alcohol in the aqueous phase is a prerequisite for successful emulsification. Indeed, dissolution

Table 4
Recipes for miniemulsifications

MINI-Emulsification number	Polymer			Heptane (g)	Water (g)	Surfactants[a]	
	Type	Amount (g)	Weight fraction in the latex (%)			Type	Amount (g)
M1	Lucant® HC-20 + EPDM 99488K	30.0 + 10.1	21.3	10.0[b]	135.6	SDBS + cetyl alcohol	1.0 + 1.3
M2	Lucant® HC-20 + EPDM 99488K	30.1 + 10.2	21.4	10.0[c]	135.6	SDBS + hexadecane	0.9 + 1.2

[a] Concentration of SDBS in water = 2×10^{-2} mol dm^{-3} and Concentration of costabilizer in water = 4×10^{-2} mol dm^{-3}.

[b] Weight fraction of organic phase in latex M1: 26.6 wt%.

[c] Weight fraction of organic phase in latex M2: 26.7 wt%.

of cetyl alcohol in the oil phase before addition to the aqueous phase causes instantaneous destabilization of the emulsion after cessation of stirring. Therefore, cetyl alcohol was added in a first step to the aqueous solution of SDBS. In a subsequent step, the cetyl alcohol/water/SDBS mixture was stirred for 2 h at 65 °C to promote the dissolution of cetyl alcohol. After cooling down the mixture to room temperature, the solution was subjected to pulsed ultra-sonification (sonicating probe 400W, Dr Hielscher UP400S) for 1 min with an amplitude of 50%, in order to enhance the formation of mixed emulsifier liquid crystalline structures. The latter structures are believed to improve emulsifier adsorption and emulsion stability. In a last step, the organic phase, consisting of a neat polymer or a polymer diluted with *n*-heptane, was added to the aqueous phase. An emulsion with submicron polymer particles was obtained by stirring with the Ultra-Turrax® at 24,000 rpm, followed by particles shearing in the homogenizer at 300 bar.

3. Results and discussion

3.1. Optimization of the surfactant system

The first experiments, concerning conventional emulsifications, were carried out with the Lucant® HC-20 ethylene–propylene copolymer and different types of emulsifier. Particle size distributions obtained for emulsions E1 to E4 are shown in Fig. 1. By using SDBS as surfactant, particles with an average diameter of 350 nm can be obtained (latex E1). However, a bimodal particle size distribution was observed, with a secondary peak around 2 μm. This peak was present in all our studied systems, except in latex E4. In this formulation, Brij 700 was used as emulsifier. With Brij 700, particles with an average diameter of 430 nm were obtained. The better stabilization obtained with Brij 700 may be explained by its high hydrophilic–lipophilic balance (HLB), being 18.8 (Table 1). The HLB value represents the tendency of an emulsifier to act as an oil-soluble or as a water-soluble type of

emulsifier [24]. A low HLB, e.g. 1–9, indicates an oil-soluble substance, while a high HLB, e.g. 11–20, suggests a water-soluble compound. Lipophilic emulsifiers are typically nonionic, such as sorbitan trioleate (HLB = 1.8) or propylene glycol monolaurate (HLB = 4.5), as well as the saturated and unsaturated fatty acids. On the other hand, hydrophilic emulsifiers are typically ionic, such as soaps of alkyl or aryl sulfuric acids, e.g. sodium lauryl sulfate or sodium dodecyl sulfate, or soaps of alkyl or aryl sulfonic acids, e.g. sodium dodecyl benzene sulfonate (HLB = 11.7).

Moreover, for nonionic surfactants, the HLB value is also related to the ethoxylation level of the surfactant, namely the ethylene oxide content, which represents the water-soluble portion of the surfactant molecule. As a consequence, more ethylene oxide units lead to a higher water-solubility and a higher HLB value.

In the present work, Brij 700 possesses the highest ethoxylation level of the surfactants used, hence the highest HLB value. Its use will enhance steric stabilization of the latex particles, compared to the other surfactants, since its long hydrophilic chain will generate the longest distances between particles.

As explained earlier, Ostwald ripening often leads to the destabilization of a latex. To avoid this phenomenon, the miniemulsification principle may help. Thus, polymer diffusion from small to larger particles would be retarded due to the presence of a costabilizer. However, the principle of retardation of polymer transport from small to larger particles is only operative for systems with polymers that are slightly water soluble [25,26]. Because EP(D)M can be regarded as completely insoluble in water, Ostwald ripening is not very likely the reason for the 2 μm particles observed.

Nevertheless, hexadecane and cetyl alcohol were employed to further understand the mechanisms involved in the stabilization of the submicron particles. Fig. 2 represents a comparison of the particle size distributions
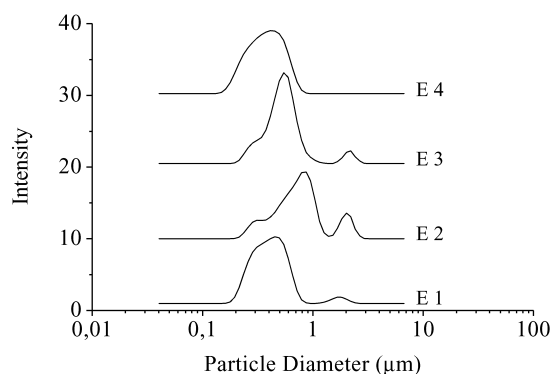

Fig. 1. Influence of the nature of the surfactant on the particle size distribution of EPM HC-20 latices: SDBS (E1), Brij 97 (E2), Igepal CO-890 (E3), and Brij 700 (E4).
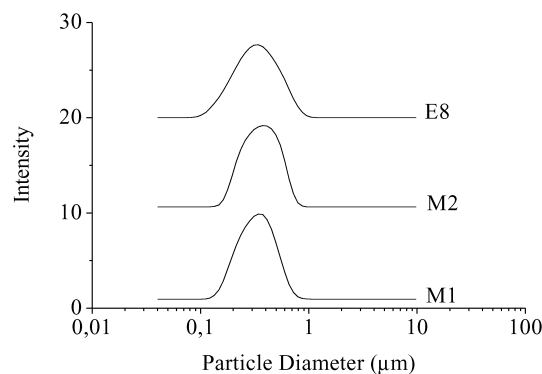

Fig. 2. Particle size distribution obtained for latices based on mixtures of EPM HC-20 and EPDM 99488K, and made by miniemulsification with SDBS/cety alcohol (M1) or with SDBS/hexadecane (M2), or by conventional emulsification with an equimolar mixture of SDBS and Brij 700 (E8).

obtained for latices based on mixtures of EPM HC-20 and EPDM 99488K (polymers P1 and P3) produced either with the conventional emulsification or with the miniemulsification route.

Both costabilizers, i.e. hexadecane and cetyl alcohol, lead to similar particle size distributions and to volume-average diameters of 360 nm. A good latex stability was provided by the surfactant combinations SDBS/hexadecane and SDBS/cetyl alcohol, for a period exceeding at least three weeks, completely suppressing the peak at 2 μm.

It has been observed that an efficient surfactant, i.e. steric (Brij 700, Fig. 1) or electrostatic (SDBS, Fig. 2) is necessary to ensure the colloidal stability of submicron EP(D)M latices. However, SDBS alone (Fig. 1) is not able to avoid the existence of 2 μm particles after homogenizing at 300 bar. Our results point to the length of the hydrophobic moiety to be a key parameter in the emulsification process. In order to emphasize the role of the aliphatic part of the stabilizing system, a study was carried out with Brij 97 as surfactant. The hydrophobic tail of both Brij 700 and Brij 97 consists of a succession of 18 carbon atoms. However, as observed on Figs. 1 and 3, the use of Brij 97 did not lead to a colloidally stable latex with a monomodal particle size distribution. As explained earlier, the hydrophilic head of Brij 97 is too short to act as an efficient steric stabilizer. However as shown in Fig. 3, an equimolar mixture of Brij 97 and SDBS leads to a monomodal particle size distribution and a volume-average diameter of 420 nm.

Therefore, 2 μm particles can be avoided using a combination of SDBS and Brij 97 (Fig. 3), of SDBS and hexadecane or cetyl alcohol (Fig. 2), or with Brij 700 alone (Fig. 1). In all those systems, an efficient colloidal stability was provided by either steric or electrostatic repulsions, and the presence of 2 μm particles was avoided by a long hydrophobic chain.

The long aliphatic part, i.e. consisting of a succession of at least 16 carbon atoms, may act as a co-solvent for the EP(D)M. Thus, polymer coils are partly swollen by the costabilizer or by the hydrophobic tail of the surfactant. So

the viscosity of the particles is reduced, facilitating the formation of submicron particles.

Since Brij 700 and SDBS were, respectively, able to avoid the existence of 2 μm particles and to produce particles with an average diameter of 350 nm, mixtures of both surfactants were then investigated in order to achieve the most suitable surfactant system. The molar ratio of emulsifier and EP(D)M was kept constant; the molar ratio of SDBS and Brij 700 was the only variable parameter. The influence of the SDBS/Brij 700 molar ratio on the particle size distribution of EPM HC-20-based latices is shown in Fig. 4. The best result was obtained for latex E6 stabilized with an equimolar mixture of SDBS and Brij 700. A monomodal particle size distribution was obtained, the volume-average particle diameter being 360 nm. This latex remained colloidally stable for at least two months.

3.2. Influence of polymer viscosity on particle size distribution

According to literature [4], the main criterion for successful emulsification of a polymer is the low viscosity of the cement: above a polymer viscosity of 10 Pa s at room temperature, emulsification is hardly possible. Burton and O'Farrell were able to produce a latex containing submicron particles with a cement exhibiting a viscosity of 1.5 Pa s. Unfortunately, no experimental details about shear rate or pressure during the homogenizing step were mentioned.

For the present work, five polymers (Table 2) were used to determine the influence of the polymer viscosity on the particle size distribution of the obtained artificial latices.

As shown in Fig. 4, the apparent viscosity of the polymers does not significantly depend on the shear rate, indicating that all polymers behave like Newtonian fluids. Viscosities range from 0.5 Pa s to 10^6 Pa s at 20 °C.

Burton and O'Farrell's statement [4] regarding the required viscosity of a polymer for its successful emulsification has been verified. As expected, the high viscosities of pure polymers P2 to P5 forbid their emulsification into stable dispersions of submicron particles in water. Polymer
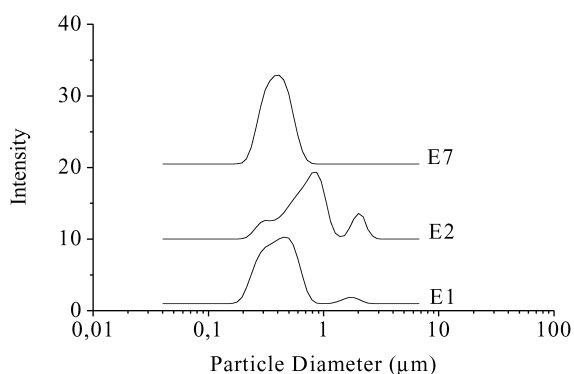

Fig. 3. Particle size distribution of EPM HC-20 latices stabilized with: SDBS (E1), Brij 97 (E2), equimolar mixture of SDBS and Brij 97 (E7).
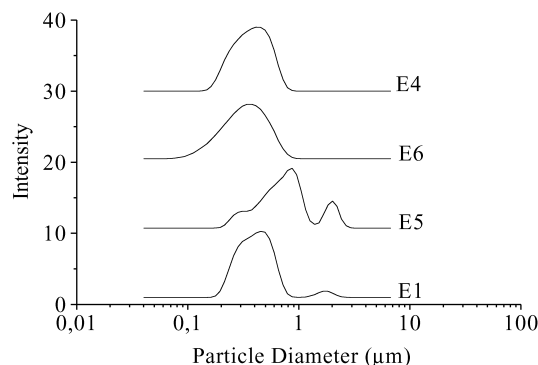

Fig. 4. Influence of SDBS/Brij 700 molar ratio on the particle size distribution of EPM HC-20 latices. The latices are made with the following molar ratios: 100/0 (E1), 90/10 (E5), 50/50 (E6), and 0/100 (E4).

Table 5
Polymer solutions used for viscosity measurements

Cement	EPM HC-20 (wt%)	EPDM 99488K (wt%)	*n*-heptane (wt%)	Viscosity (Pa s)
C1	–	100	–	510
C2	75	25	–	3.7
C3	94	6	–	0.9
C4	100	–	–	0.5
C5	60	20	20	0.3

P1 was the only polymer which could be emulsified without addition of a low-viscosity solvent, i.e. *n*-heptane.

Extensive studies on several cements based on mixtures of EPM HC-20, EPDM 99488K and *n*-heptane (Table 5) were carried out in order to determine the influence of the viscosity of the polymer solution on the emulsification process. All cements obeyed Newton's law of viscosity within experimental error.

The viscosities of cements C2 to C5 are lower than 10 Pa s. Thus, successful emulsifications are expected, leading to submicron particles. However as shown in Fig. 5, only latices made of cements with viscosities lower than 1 Pa s (C3 to C5) lead to submicron particles.

As can be concluded from Table 5 and Fig. 5, particle size distributions and average diameters of the studied latices are not significantly related to the nature of the polymer. In contrast, the cement viscosity plays a dominant role in the emulsification of the polymer (Fig. 6). Indeed, a cement with a viscosity ranging from 1 to 10 Pa s can easily be emulsified. However, submicron particles will be hard to obtain at 300 bar. Reduction of cements viscosities to values lower than 1 Pa s leads to easy emulsification and to submicron particles with a volume-average diameter of 360 nm. This phenomenon may be explained by the decrease of the entanglement density [27] with decreasing viscosity and molecular weight. A higher molecular weight leads, for linear copolymers, to longer chains and to higher
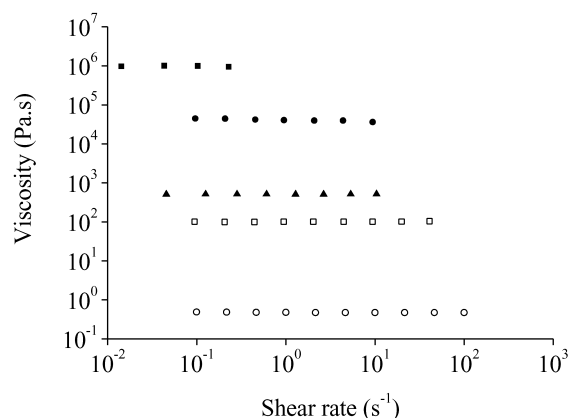

Fig. 5. Viscosity of the pure polymers measured at 20 °C as a function of shear rate. The polymers used are P1 (○, $\eta = 0.5$ Pa s), P2 (□, $\eta = 100$ Pa s), P3 (▲, $\eta = 510$ Pa s), P4 (●, $\eta = 42,500$ Pa s), and P5 (■, $\eta = 106$ Pa s).
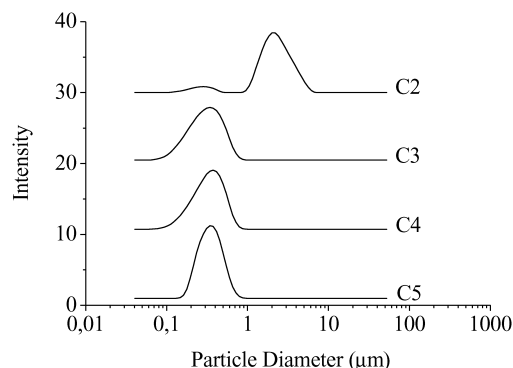

Fig. 6. Influence of cement viscosity on particle size distribution of latices based on cements C2 ($\eta = 3.7$ Pa s), C3 ($\eta = 0.9$ Pa s), C4 ($\eta = 0.5$ Pa s), and C5 ($\eta = 0.3$ Pa s).

viscosities. These chains tend to form many physical entanglements that determine the fixed macroscopic morphology of the particles, counteracting deformation and further breaking up.

The present work points out that EPDM viscosities in the range of 1 to 10 Pa s still result in too many entanglements per molecule. On the other hand, for similar polymers with viscosities below 1 Pa s, the homogenizing step of the emulsification, at a pressure of 300 bar and with a shear rate of $3.2 \times 10^7 \, \text{s}^{-1}$, is facilitated by a lower entanglement density.

4. Conclusion

The emulsification of low molecular weight EP(D)M requires the presence of two important stabilizing parts: an efficient surfactant and a species with a long alkyl chain. The surfactant, steric or electrostatic, ensures the colloidal stability of the obtained latex. The long aliphatic chain, i.e. the hydrophobic tail of the surfactant or the costabilizer, probably acts as a co-solvent to 'swell' the polymer and helps the breaking-up of the particles during the homogenizing step.

Therefore, low molecular weight EP(D)M can be successfully emulsified without addition of organic solvent, either by using a conventional method of preparation of artificial latices or by using a miniemulsification procedure. For the conventional procedure, the best result has been obtained with a combination of electrostatic (anionic surfactant, SDBS) and steric (nonionic surfactant, Brij 700) stabilization. For miniemulsification, SDBS has been used in combination with hexadecane or cetyl alcohol.

In all recipes leading to stable emulsions, a monomodal particle size distribution and an average diameter of 360 nm were obtained.

An important parameter, in addition to the choice of the emulsifier system, is the viscosity of the polymer. It has been demonstrated that the viscosity of the elastomer has to be lower than 1 Pa s at 20 °C for proper production of

submicron particles by high shear stirring followed by homogenization at high pressure (300 bar) and with high shear rate ($3.2 \times 10^7 \, s^{-1}$).

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