Synthesis of colloidally stable lattices nano-rubber particles based on natural rubber (cis-1,4-polyisoprene)

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ABSTRACT

The best impact modifiers for coatings and engineering plastics include fixed morphology core-shell particles. For the present work, natural rubber (cis-1,4-polyisoprene) was chosen, for its elasticity, resilience, and toughening effect for most brittle materials and has been used to prepare the core of the desired particles. The solution-emulsification technique was used to produce artificial latices based on natural rubber (cis-1,4-polyisoprene). Conventional emulsification techniques as well as 'miniemulsification' methods have been investigated. In both cases, a larger volume of polymer is reduced into tiny rubber balls in the nano scale using an ultrasonic homogenizer. The difference between conventional emulsification and miniemulsification resides in stabilizing the system. For the conventional emulsification method, an equimolar mixture of anionic (Potassium palmitate) and nonionic (polyoxyethylene (100) stearyl ether, Brij 700) surfactants was found to be the optimal surfactant system. For the miniemulsification method, a combination of Potassium palmitate as a surfactant and hexadecane or cetyl alcohol as a 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.

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INTRODUCTION

Natural rubber (cis-1,4-polyisoprene) has an outstanding resilience and tensile strength, as well as low heat build-up. In addition, natural rubber latex has excellent tack (that is, the ability to stick to itself and to other materials), which makes it best suited for pressure-sensitive adhesives, and excellent water resistance (whereas some synthetics absorb water)[1]. Because of its elasticity, resilience, and toughening effect, natural rubber (NR) is the basic constituent of many products used in the transportation, industrial, consumer, hygienic and medical sectors.

Of these major end-use markets for rubber,

toughening of brittle materials and transportation are by far the largest two sectors, with tires and tire products accounting alone for over 50% of NR consumption. Truck and bus tires would represent the largest single outlet for NR, followed by automobile tires. However, a drawback of polyisoprene is that it has a moderate environmental resistance to factors such as oxidation and ozone; so too for its scarce resistance to chemicals, including gasoline, kerosene, hydraulic fluids, degreasers, synthetic lubricants, and solvents.

To overcome the aforementioned drawback; in this paper; natural rubber (cis-1,4-polyisoprene) has been emulsified to form a stable colloid that was then crosslinked in the nano scale forming a stable, elastic, resilient nano rubber particles for toughening of brittle materials. The particle size control, degree of crosslinking, colloidal stability, and toughening properties of polyisoprene make it an important industrial polymer, suitable for use in many applications.

Generally, the mechanical properties of rigid (brittle) materials are enhanced by the introduction of a dispersed rubbery phase. This "toughening" procedure[2] is commonly applied to increase material resistance to cracking/fatigue at low temperatures and to boost stability with minimum creep at higher temperatures in almost every high performance structure materials, including thermoplastic and thermoset polymers[3], asphalt[4], and composite products[5]. The most convenient process is by blending elastomer with rigid material in melt or solution with or without an interfacial agent to control morphology and interfacial adhesion. Core-shell morphology[6], having a cross-linked rubber core and a grafted shell connecting the rubber particle with the rigid matrix, is an ideal structure for achieving toughness. Many examples, including HIPS (high impact polystyrene), ABS engineering plastic[7], and rubber-toughened expoxy resins, exhibit both high impact strength and good rigidity and make them the materials of choice for many applications.

In this research, we have developed a new class of rubber particles which are completely processible in melt and solution, and can be directly applied in toughening a broad range of rigid materials by reactive extrusion, mixing, and *in situ* polymerization processes. The *in situ* formed core-shell rubber particle structure is an imperative technological advancement that will catalyze the evolution of engineering materials which significantly effect and better the way we live.

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 (styreneacrylonitrile), 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, ethylene–propylene copolymers (EPM), and ethylene–propylene–diene monomer (EPDM) as well as polydienes. An example of the latter is cis-1,4-polyisoprene which is the preferred elastomer for application as impact modifier for coatings and engineering plastics.

A dispersion of polyisoprene in water is obtained through the preparation of an artificial latex, i.e. a pre-formed polymer colloidally dispersed in an aqueous medium[8]. 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[9] has been employed by Yang et al.[10] 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, 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[11], can be used. It consists of the dissolution of the polymer in a volatile solvent to form a solu-

tion 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 nano (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 lattices[12]. Electrostatic stability is provided by ionic surfactants as described in the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory[13]. The coverage of the particles by charged species creates an electric double layer, leading to electrostatic repulsion. Steric stabilization[14] 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[15]. 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. Colombie et al.[16] 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[17] in the emulsion polymerization of styrene.

With respect to the colloidal stability; the term miniemulsion describes a nano (submicron) oil-in-water dispersion with colloidal stability ranging from hours to months[18]. A practical application of the procedure to produce miniemulsions, i.e. miniemulsification, is found in the preparation of artificial latices from polymer solutions, as reported by El-Aasser[19]; it is the process of dispersing a polymer in water, stabilized by a combination of an anionic surfactant and a costabilizer. 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[20]. 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[20] 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[21] used styrene as monomer and hexadecane as costabilizer, while Rodriguez[22] used styrene and methyl methacrylate with both hexadecane and cetyl alcohol.

Finally, an important factor controlling the colloidal stability is the viscosity of the dispersed phase which

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TABLE 1 : Description of the surfactants

Name	Description	HLB	Mn
Potassium palmitate	Palmitic acid potassium salt	6	294
SDS	Sodium dodecyl sulfate	8	288
Brij 30	Polyoxyethylene (4) lauryl ether	9	362
Brij S10	Polyoxyethylene (10) stearyl ether	12	711
Brij 700	Polyoxyethylene (100) stearyl ether	19	4970
IGEPAL DM-970	Polyoxyethylene (150) dinonylphenyl ether	19	---

TABLE 2 : Recipes for conventional emulsifications

Sample	Type	Amount (g)
A1	Potassium palmitate	0.9
A2	Brij S10	1.8
A3	IGEPAL DM-970	5.0
A4	Brij 700	12.1
A5	Potassium palmitate + Brij 700 (90–10)	0.8 + 1.2
A6	Potassium palmitate + Brij 700 (50–50)	0.4 + 6.0
A7	Potassium palmitate + Brij S10 (50–50)	0.5 + 0.9
A8	Potassium palmitate + Brij 700 (50–50)	0.4 + 6.2

In all cases: (Emulsifier/Polyisoprene) X 100 ≈ 10.0 wt% , polymer = 10 g, water = 50 mL

represents another key parameter for the emulsification of a polymer. According to Burton and O'Farrell[11], 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[23] to produce high molecular weight polyisoprene 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 the least amount of non water-miscible solvents in order to minimize the amount of solvent that has to be removed. 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, hexane, heptane).

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 polyisoprene-based latices will be emphasized. Finally, the influence of the cement viscosity on the emulsification process will be discussed.

EXPERIMENTAL

Chemicals

Surfactants, n-hexane, toluene, hexadecane, and cetyl alcohol are all from Aldrich and were used as received. Deionized water was used for all latices. The characteristic descriptions of the surfactants used in this study are summarized in TABLE 1.

Divinylbenzene and isoprene as crosslinkers (Aldrich) were dried and vacuum distilled over calcium hydride. Polyisoprene (NR; Narobien), benzoyl peroxide (BPO, Fluka, 75 %), methylene bis acryl amide (MBA), potassium hydroxide KOH, sodium hydroxide NaOH and methanol were used as received.

Characterization of polymers

(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

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) Viscosities

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

Characterization of lattices-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 theo-

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ries, to determine particle size distributions. Moreover, the range of detectable particle sizes is extended to the submicron region (lower size limit: 50 nm of diameter).

Preparation of artificial latices from polyisoprene

(1) Conventional emulsification

Recipes are collected in TABLE 2. If necessary, the first step involved the dissolution of the polymer in n-hexane 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. The size of the eventually swollen polymer particles was reduced by processing the emulsion product in an ultrasonic homogenizer for times ranged from 1 to 3 h, depending on the viscosity of the samples.

(2) Miniemulsification

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.[24], the initial presence of cetyl alcohol in the aqueous phase is a prerequisite for successful emulsification. Indeed, dissolution 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 water phase. In a subsequent step, the cetyl alcohol/water 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 ultrasonification (sonicating probe 750W) for 1 min with 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-hexane, was added to the aqueous phase. An emulsion with submicron polymer particles was obtained by stirring with a mechanical rotor, followed by particles shearing in the homogenizer at 300 bars.

RESULTS AND DISCUSSION

Optimization of the surfactant system

The first experiments, concerning conventional emulsifications, were carried out with polyisoprene and different types of emulsifier. Particle size distributions obtained for emulsions A1 to A4 are shown in figure 1. By using Potassium palmitate as surfactant, particles with an average diameter of 450 nm (main peak) can be obtained (latex A1). However, a tri-modal particle size distribution was observed, with two additional peaks around 80 nm and 2.5 μm. Some of these extra peaks were 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 530 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[25]. 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 such as palmetic acid. 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.

The Hydrophilic-lipophilic balance of a surfactant is a measure of the degree to which it is hydrophilic or lipophilic, determined by calculating values for the different regions of the molecule, as described by Griffin in 1949[26] and 1954[27]. Other methods have been suggested, notably in 1957 by Davies[28]. The easist one is Griffin's method that is applicable for non-ionic surfactants as described in 1954 works as follows:
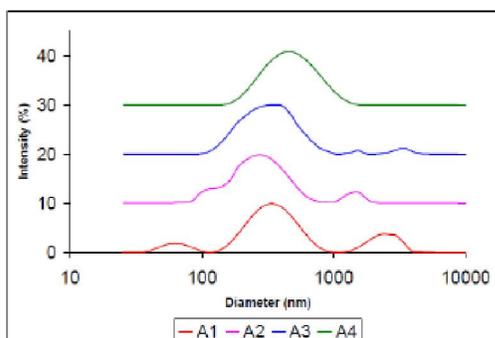
Figure 1 : Influence of the nature of the surfactant on the particle size distribution of polyisoprene latices: Potassium palmitate (A1), Brij S10 (A2), IGEPAL DM-970 (A3), and Brij 700 (A4)
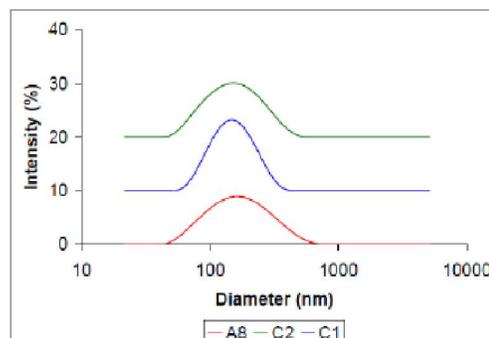
Figure 2 : Particle size distribution obtained for latices based on polyisoprene and made by miniemulsification with potassium palmitate /cety alcohol (C1) or with potassium palmitate /hexadecane (C2), or by conventional emulsification with an equimolar mixture of potassium palmitate and Brij 700 (A8)
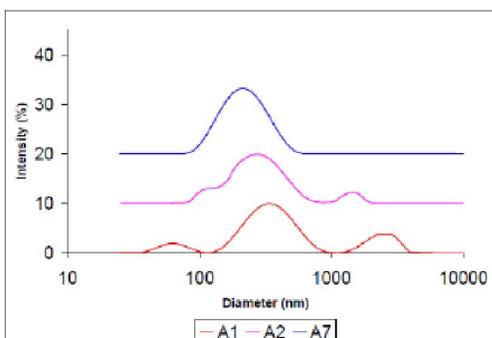
Figure 3 : Particle size distribution of polyisoprene latices stabilized with: potassium palmitate (A1), Brij S10 (A2), equimolar mixture of potassium palmitate and Brij S10 (A7)
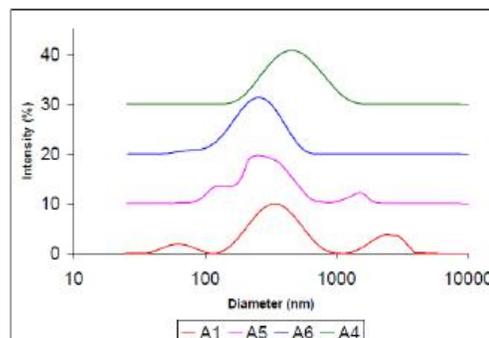
Figure 4 : Influence of potassium palmitate /Brij 700 molar ratio on the particle size distribution of polyisoprene latices. The latices are made with the following molar ratios: 100/0 (A1), 90/10 (A5), 50/50 (A6), and 0/100 (A4)

HLB = 20* M_h / M

where M_h is the molecular mass of the hydrophilic portion of the Molecule, and *M* is the molecular mass of the whole molecule, giving a result on an arbitrary scale of 0 to 20. An HLB value of 0 corresponds to a completely hydrophobic molecule, and a value of 20 would correspond to a molecule made up completely of hydrophilic components.

The HLB value can be used to predict the surfactant properties of a molecule:

- A value from 0 to 3 indicates an anti-foaming agent
- A value from 4 to 6 indicates a W/O emulsifier
- A value from 7 to 9 indicates a wetting agent
- A value from 8 to 18 indicates an O/W emulsifier
- A value from 13 to 15 is typical of detergents
- A value of 10 to 18 indicates a solubiliser or hydrotrope.

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 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 co stabilizer. However, the principle of retardation of a polymer transports from small to larger particles is only operative for systems with polymers that are slightly water soluble[29]. Because polyisoprene can be regarded as completely insoluble in water, Ostwald ripening is not very likely the reason for the 2.5 μm particles observed.

Nevertheless, hexadecane and cetyl alcohol were employed to further understand the mechanisms involved

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in the stabilization of the submicron particles. Figure 2 represents a comparison of the particle size distributions obtained for latices produced either with the conventional emulsification or with the miniemulsification route.

Both co stabilizers, i.e. hexadecane and cetyl alcohol, lead to similar particle size distributions and to volume average diameters of 250 nm. A good latex stability was provided by the surfactant combinations potassium palmitate/hexadecane and potassium palmitate/cetyl alcohol, for a period exceeding at least two weeks, completely suppressing the peak at 2.5 μm.

It has been observed that an efficient surfactant, i.e. steric (Brij 700, Figure 1) or electrostatic (potassium palmitate, Figure 2) is necessary to ensure the colloidal stability of submicron polyisoprene latices. However, potassium palmitate alone (Figure 1) is not able to avoid the existence of 2.5 μm particles after homogenizing at 300 bars. 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 S10 as surfactant. The hydrophobic tail of both Brij 700 and Brij S10 consists of a succession of 18 carbon atoms. However, as observed on figsure 1 and 3, the use of Brij S10 did not lead to a colloidally stable latex with a monomodal particle size distribution. As explained earlier, the hydrophilic head of Brij S10 is too short to act as an efficient steric stabilizer. However as shown in figure 3, an equimolar mixture of Brij S10 and potassium palmitate leads to a monomodal particle size distribution and a volume-average diameter of 350 nm. Therefore, 2.5 μm particles can be avoided using a combination of potassium palmitate and Brij S10 (Figure 3), of potassium palmitate and hexadecane or cetyl alcohol (Figure 2), or with Brij 700 alone (Figure 1). In all those systems, an efficient colloidal stability was provided by either steric or electrostatic repulsions, and the presence of 2.5 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 polyisoprene. Thus, polymer coils are partly swollen by the co stabilizer 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 potassium palmitate were, respectively, able to avoid the existence of 2.5 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 polyisoprene was kept constant; the molar ratio of potassium palmitate and Brij 700 was the only variable parameter. The influence of the potassium palmitate / Brij 700 molar ratio on the particle size distribution of polyisoprene based latices is shown in figure 4. The best result was obtained for latex A6 stabilized with an equimolar mixture of potassium palmitate and Brij 700. A monomodal particle size distribution was obtained, the volume-average particle diameter being 420 nm. This latex remained colloidally stable for at least a month.

CONCLUSION

The emulsification of natural rubber (polyisoprene) 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 co-stabilizer, probably acts as a co-solvent to 'swell' the polymer and helps the breaking-up of the particles during the homogenizing step.

Therefore, polyisoprene 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, potassium palmitate) and steric (nonionic surfactant, Brij 700) stabilization. For miniemulsification, potassium palmitate 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 350 nm were obtained.

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