

Eudragit[®]-PEG Nanoparticles: Physicochemical Characterization and Interfacial Tension Measurements

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Abstract

The objectives of this study are to understand the mechanisms involved in the stabilization of water/oil interfaces by polymeric nanoparticles (NPs) (Eudragit[®]). Eudragit L100 NPs of various sizes and Zeta potentials were studied and compared at a water/cyclohexane model interface using a droplet tensiometer (Tracker Teclis, Longessaigne, France). The progressive interfacial adsorption of the NPs in the aqueous phase was monitored by tensiometry. The model interface was maintained and observed in a drop tensiometer, analyzed via axisymmetric drop shape analysis (ADSA), to determine the interfacial properties. Given the direct relationship between the stability of Pickering emulsions (emulsions stabilized by solid nanoparticles) and the interfacial properties of these layers, different nanoparticle systems were compared. Specifically, Eudragit NPs of different sizes were examined. Moreover, the reduction of the Zeta potential with PEG-6000 induces partial aggregation of the NPs (referred to as NP flocs), significantly impacting the stability of the interfacial layer. Dynamic surface tension measurements indicate a significant decrease in interfacial tension with Eudragit[®] nanoparticles (NPs). This reduction correlates with the size of the NPs, highlighting that this parameter does not operate in isolation. Other factors, such as the contact angle and wettability of the nanoparticles, also play a critical role. Notably, larger NPs further diminished the interfacial tension. This study enhances our understanding of the stability of Pickering emulsions stabilized by Eudragit[®] L100 polymeric na-

noparticles.

Keywords

Nanoparticles, Eudragit®, PEG, Interfacial Tension, Pickering Emulsion

1. Introduction

Over the last two decades, nanotechnology has garnered significant interest across various research fields for its ability to develop nanoscale materials. These materials are produced using diverse techniques, categorized broadly into physical or chemical methods. Owing to their size, which ranges from approximately 1 to 100 nm, nanoparticles exhibit specific and controllable properties that distinguish them from their macroscopic counterparts, thus paving the way for unique applications [1] [2] [3]. The alteration in properties is attributed to two primary effects: surface effects or size reduction effects, where a decrease in particle size increases the proportion of atoms on the surface; and quantum modification effects, which alter the electronic structure [1] [4]. The ratio of surface atoms to bulk atoms escalates significantly as particle size diminishes. Given that surface atoms exhibit reduced coordination compared to their bulk counterparts, nanostructured materials display markedly different physical, chemical, optical, mechanical, electrical, and therapeutic properties [2] [5]. Modification of surface atoms contributes significantly to the unique characteristics of nanoparticles (NPs) [6]. Therefore, nanoscale materials hold great promise for applications across various technological fields, including medicine, nanoelectronics, computing, aeronautics, space exploration, biotechnology, and agriculture [1] [6]. Nanoparticle systems have enabled the design of nanoparticles that protect the active principle from premature degradation while also controlling its release in terms of location and duration. This spatio-temporal control is achieved through innovative concepts in chemistry and physico-chemistry, coupled with the development of novel materials in pharmaceutical physics and galenics [7].

The use of nanoparticulate systems composed of polymers holds significant promise for treating serious diseases and can also stabilize emulsions or nanoemulsions [8]. Emulsions are metastable dispersed systems comprising at least two immiscible liquids and an amphiphilic agent, where one of the liquids is dispersed in the second in the form of small spherical drops. The size of these drops varies depending on conditions, from 0.1 to several tens of micrometers. Unlike emulsions, nanoemulsions are ultrafine dispersions, leading to the formation of nanometric-sized droplets (20 - 300 nm). This size range enables nanoemulsions to resist physical destabilization caused by gravitational separation (sedimentation, creaming), flocculation, and/or coalescence. Both systems are not thermodynamically stable; the most stable state would involve macroscopic separation of the two fluids. Traditionally, surfactant molecules have been used

to stabilize these systems. However, surges in environmental protection awareness, safety considerations, implementation ease, and cost constraints are prompting a re-evaluation of emulsions stabilized by surfactants. We are moving towards the gradual elimination of organic solvents and synthetic surfactants, both of which are considered harmful to the environment [7] [9] [10] [11]. At the beginning of the last century, Ramsden and Pickering [12] [13] demonstrated the feasibility of emulsions without surfactants, using solid particles instead. These emulsions, known as “Pickering Emulsions,” are enjoying renewed interest today due to their numerous advantages: good stability, environmental protection, user safety, and a variety of particle types. As a result, they have been adopted by several industrial sectors including pharmacy, cosmetics, food processing, and chemistry to achieve desirable usage properties or compositions. Additionally, one of the primary benefits of Pickering emulsions is their enhanced stability compared to other types of emulsions. The adsorption of solid particles at the oil-water interface is almost irreversible and strong. This leads to the formation of a dense film that encases the droplets, significantly reducing their likelihood of coalescing. Recently, the potential for emulsions and nanoemulsions stabilized by Eudragit® polymeric nanoparticles has been demonstrated [8]. This formulation could serve as a promising system for encapsulating therapeutically relevant molecules, facilitating the controlled and targeted release of the active principle from the internal phase. The aim of the research presented in this manuscript was to synthesize polymeric nanoparticles of Eudragit L100 (an anionic copolymer) through spontaneous nanoemulsification and to characterize them physicochemically, enabling the subsequent production of a Pickering nanoemulsion stabilized by these polymeric nanoparticles.

2. Materials and Methods

2.1. Materials

HPLC-grade cyclohexane, acetone, ethanol, and polyethylene glycol 6000 (PEG-6000) were acquired from Sigma-Aldrich (Saint Louis, USA). Anionic copolymers based on methacrylic acid and methyl methacrylate (1:1) (Eudragit L100) were sourced from Evonik Roehm, Darmstadt, Germany. Ultrapure water was generated using the Milli-Q filtration system (Millipore, Saint-Quentin-en Yvelines, France). We also utilized Acrodisc Syringe Filters with Nylon Membrane, provided by PALL life sciences (USA). All chemicals employed were of analytical grade.

2.2. Methods

2.2.1. Synthesis of Eudragit®-PEG Nanoparticles

The synthesis method employed is known as “spontaneous nano-emulsification.” This method begins with the preparation of a homogeneous organic solution containing water-miscible organic solvents (such as acetone and ethanol) and Eudragit®. This solution is subsequently injected into an aqueous phase enriched

with a dispersant and stabilizer, such as PEG-6000, under continuous stirring. The process concludes with the solvents being evaporated at 40°C under reduced pressure (175 atm for ethanol and acetone) using a Büchi rotavapor. This evaporation step facilitates the recovery of an aqueous suspension of polymeric nanoparticles. The Eudragit L100-PEG-6000 weight-to-weight (w/w) ratios explored in this study were 1:1, 1:2, 1:3, 1:5, and 1:6, corresponding to Eudragit® to PEG ratios of 1, 0.5, 0.33, 0.2, and 0.16, respectively.

2.2.2. Nanoparticles Characterization

Size distributions and the polydispersity index (PDI) were analyzed using dynamic light scattering (DLS) and ζ potential measurements with a NanoZS® Malvern apparatus (Malvern, Orsay, France). The apparatus utilized a helium/neon laser (4 mW) operating at 633 nm, with the scatter angle set at 173° and the temperature controlled at 25°C. For the analysis of DLS data, a cumulant-based method was employed. ζ potential measurements were conducted immediately after formulation to determine the electrophoretic mobility of the particles, employing the Henry's equation under the Smoluchowski approximation. All experiments were conducted in triplicate.

2.2.3. Dynamic Interfacial Tension Measurements

The dynamic interfacial tension (γ) was measured using a drop tracker tensiometer (Tracker Teclis, Longessaigne, France) based on the ADSA method [14]. This process involved forming and maintaining a rising drop of cyclohexane in a thermostatically controlled cell filled with an aqueous phase containing polymeric nanoparticles. The drop's shape was continuously recorded with a video camera, enabling the determination of the interfacial area and surface tension through its Laplacian form. All experiments were conducted at 25°C and replicated three times.

3. Results and Discussion

3.1. Eudragit®-PEG Nanoparticles Characterization

The synthesis of nanoparticles was carried out through spontaneous nanoemulsification, a widely adopted low-energy method for nanoparticle synthesis. This process involves an abrupt shift of solvents such as acetone and ethanol to an aqueous phase, leading to the formation of nanoparticles [15] [16] [17]. **Figures 1(a)** and **Figure 1(b)** illustrate the size distribution of Eudragit® nanoparticles based on Eudragit/polyethylene glycol (PEG) combinations (1:1 and 1:6) and the evaluation of the nanoparticles' hydrodynamic diameter as influenced by the Eudragit®/PEG ratio, respectively. **Figure 1(c)** represents the Polydispersity Index.

The nanoparticles were synthesized according to the Eudragit/PEG ratio used. According to Kırımlioğlu *et al.* and Dillen *et al.* [18] [19], one of the most significant physical characteristics of colloidal carriers is their particle size and distribution. The analysis depicted in **Figure 1** illustrates that the Eudragit/PEG ratio

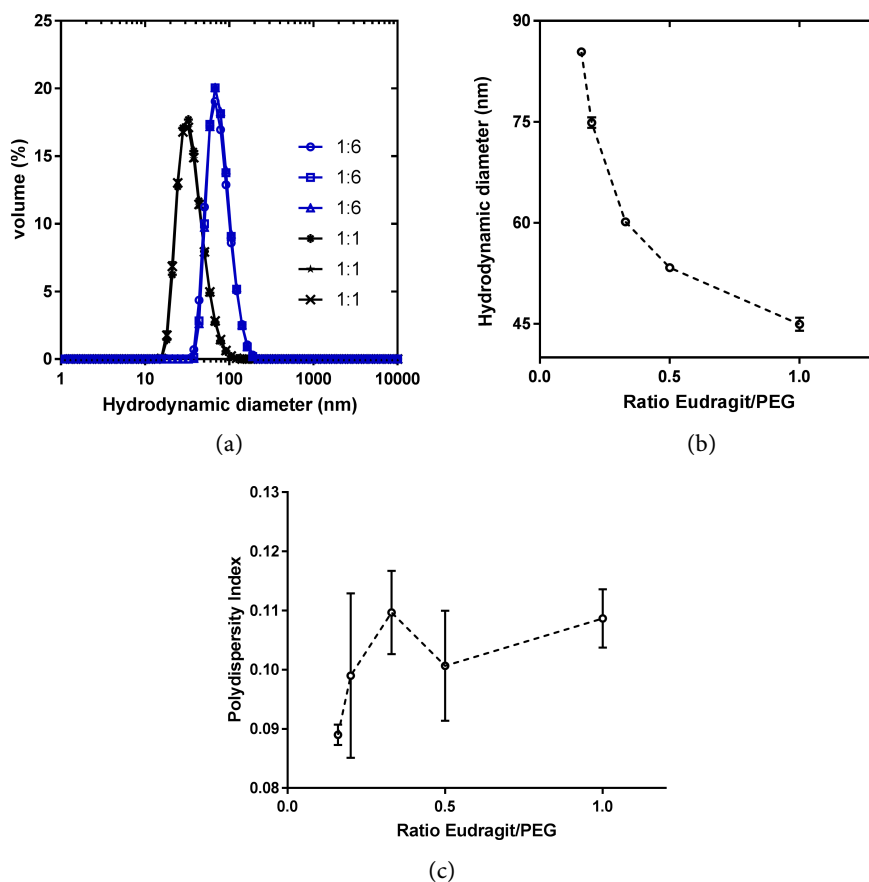


Figure 1. Hydrodynamic diameter of Eudragit®-PEG nanoparticles: (a) Size distribution by volume; (b) Evolution with ratio Eudragit/PEG; (c) Polydispersity Index.

significantly influenced the hydrodynamic diameter and the polydispersity index. In fact, PEG serves as a stabilizer. We selected it because it shows promise for in vivo applications, being a polymer with a well-established safety profile in humans [20] [21]. W.-S. Cho and colleagues synthesized spherical gold nanoparticles (AuNPs) coated with PEG. The hydrodynamic sizes of the PEG-coated AuNPs were measured at 27.6 ± 6.6 nm. The authors attributed this size to the formation of protective PEG layers covalently bonded to the AuNPs' surfaces. The presence of a PEG layer was confirmed through Fourier transform infrared (FTIR) analysis [22].

We observed a decrease in the size of the Eudragit® nanoparticles as the quantity of PEG present in the aqueous phase was reduced. The hydrodynamic diameter of the nanoparticles expanded from 85.38 nm at an Eudragit®/PEG ratio of 0.16, to 44.94 nm when the ratio was 1. Ali and Lamprecht demonstrated in their study, titled “Polyethylene glycol as an alternative polymer solvent for nanoparticle preparation,” the significant role of PEG in determining the size of polymeric nanoparticles [23].

This could be attributed to the fact that PEG reduces the negative charge on the surface of the anionic polymer. This is illustrated in **Figure 2**, where the zeta potential shifts from -46.62 mV for a Eudragit/PEG ratio of 1; to -8.94 for a

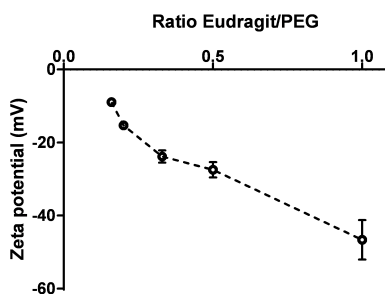


Figure 2. Evolution of nanoparticles zeta potential with ratio Eudragit/PEG.

ratio of 0.16. Indeed, the decrease in surface charge leads to diminished electrostatic repulsion between the Eudragit® nanoparticles, thus facilitating their partial agglomeration. This process of partial agglomeration or flocculation results in an increase in the size of the nanoparticles, as depicted in **Figure 1**. Our previous study involving magnesium hydroxide nanoparticles demonstrated this phenomenon of partial agglomeration through zeta potential modification [7].

This partial flocculation is explained by the increase in the polydispersity index from 0.089 to roughly 0.109 when the quantity of PEG is increased. Specifically, as nanoparticles partially agglomerate, some retain their original hydrodynamic diameter, whereas others form flocs. These flocs have a significantly higher polydispersity index.

3.2. Analysis of Dynamic Surface Tension Curves

When a new interface forms, it is initially empty, allowing each nanoparticle colliding with it to adsorb freely. At the onset of this process, there is no energy barrier between the interface and the interfacial sub-layer. This adsorption creates a concentration gradient, inducing the diffusion-controlled movement of nanoparticles from the mass towards the interfacial sub-layer, until its concentration matches that of the suspended mass. Thus, the kinetics of adsorption depends on several processes, such as diffusional transport, reorientation, and adsorption. In this work, we examined the surface dynamics of solid nanoparticles at the cyclohexane/water interface using the axisymmetric drop shape analysis method. Initially, we measured the surface tension of the interface without nanoparticles to confirm the absence of impurities. The tension values obtained ranged between 48 and 50 mN·m⁻¹ (**Figure 3**). **Figure 3** also presents a series of tensiometer measurements for Eudragit® nanoparticles (NPs) with diameters of 85, 74, 60, 53, and 44 nm.

By analyzing **Figure 3**, a sharp decrease in interfacial tension was observed for Eudragit® NPs. Thus, in the early stages of adsorption ($t \rightarrow 0$), the interfacial tension decreases rapidly. Subsequently, the decrease in interfacial tension slows down and finally reaches a dynamic equilibrium where the maximum coverage of the interface with the nanoparticles is reached ($t \rightarrow \infty$). $\gamma_{t \rightarrow \infty}$ was obtained by intercepting a curve of the variation of interfacial tension against $(1/t)^{1/2}$, as

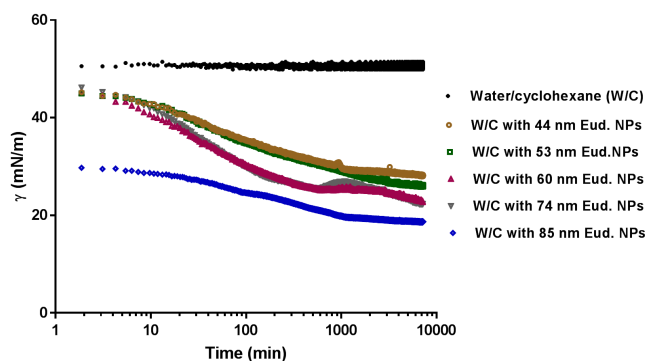


Figure 3. Cyclohexane/water interfacial tension after creation of interface in the presence of various size of Eudragit nanoparticles.

suggested by Equation (S1). This equation has been successfully used to characterize the transient behavior of surface and interfacial tension in the presence of nonionic amphiphilic molecules or macromolecules in aqueous environments, as supported by references [24] [25] [26] [27] [28].

We also noticed that this decrease was made with the increase of the size of nanoparticles. Indeed, as the size of the nanoparticles increased, the interfacial tension gradually decreased over time, eventually reaching an equilibrium value, Equation (S2), that diminishes with the increase in nanoparticle size. Specifically, with 85 nm nanoparticles, the interfacial tension decreased from 48 - 50 $\text{mN}\cdot\text{m}^{-1}$ to around 18 $\text{mN}\cdot\text{m}^{-1}$. Meanwhile, with 60 and 74 nm nanoparticles, it decreases to around 22 $\text{mN}\cdot\text{m}^{-1}$. For the smallest nanoparticles, measuring 53 and 44 nm, the interfacial tension was observed to be 26 and 28 $\text{mN}\cdot\text{m}^{-1}$ respectively, after 2 hours. Similar results were obtained by Kutuzov *et al.*, who studied the effect of cadmium selenide nanoparticles' adsorption at a water/oil interface [29]. Lin *et al.* also demonstrated that the self-assembly of particles at fluid interfaces, driven by a reduction in interfacial energy, is well established. However, for nanoscopic particles, thermal fluctuations compete with interfacial energy, leading to self-assembly that depends on the size of the particles [30]. However, it is essential to consider the hydrophilicity or hydrophobicity of nanoparticles, as these characteristics significantly impact the contact angle. Tiwari *et al.*, in an experimental study investigating the effect of silica nanoparticles (NPs) on surface tension in the presence of Triton X-100 and Tween-20 surfactants, demonstrated the role of parameters such as size and hydrophobicity, and consequently, the contact angle, in reducing interfacial tension [31].

From the results of physicochemical characterization, it is hypothesized that the zeta potential plays a significant role in the self-assembly of nanoparticles and, consequently, their adsorption at the oil/water interface. Notably, nanoparticles with the lowest zeta potential values (85 nm, -8.94) exhibited the most substantial decreases in interfacial tension. This could be attributed to their self-organization behavior. This organization plays a crucial role in the stability of Pickering emulsions by preventing coalescence between two emulsion droplets. This certainly accounts for the superior stability of Pickering emulsions in

comparison to conventional emulsions. The reduction of interfacial tension properties is also vital in stabilizing Pickering emulsions. Consequently, these nanoparticles enable the production of innovative pharmaceutical forms. These forms are not only capable of encapsulating active ingredients but also releasing them according to the pH conditions of biological environments [7] [8].

4. Conclusion

In this work, we developed Eudragit®-PEG nanoparticles with varying sizes and zeta potentials. The formulation of these nanoparticles was achieved through nano-precipitation. The aim was to characterize these Eudragit NPs on a physicochemical level and to conduct interfacial tension studies. We observed a reduction in the size of the Eudragit® nanoparticles as the amount of PEG in the aqueous phase decreased. Concurrently, there was an increase in the zeta potential from -46.62 mV to -8.94 mV when the Eudragit/PEG ratio was adjusted from 1 to 0.16. A sharp decrease in interfacial tension was also observed for Eudragit® nanoparticles (NPs). This decrease corresponded with the increase in the size of nanoparticle flocs. However, it is important to consider other parameters, such as the wetting of the nanoparticles. These properties of interfacial tension reduction are crucial for stabilizing Pickering emulsions, which, along with nano-emulsions, can offer significant pharmaceutical applications.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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Supplementary Information

$$\gamma(t)_{t \rightarrow 0} = \gamma_0 - 2RTc \left(\frac{Dt}{\pi} \right)^{1/2} \quad \text{or} \quad \left(\frac{d\gamma}{dt^{1/2}} \right)_{t \rightarrow 0} = -2RTc \left(\frac{D}{\pi} \right)^{1/2} \quad (\text{S1})$$

$$\gamma(t)_{t \rightarrow \infty} = \gamma_\infty + \frac{RT\Gamma^2}{2c} \left(\frac{\pi}{Dt} \right)^{1/2} \quad \text{or} \quad \left(\frac{d\gamma}{dt^{1/2}} \right)_{t \rightarrow \infty} = \frac{RT\Gamma^2}{2c} \left(\frac{\pi}{D} \right)^{1/2} \quad (\text{S2})$$

Ward and Tordai model