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BIODEGRADABLE MICROCAPSULES FOR BLUE DYE OF WHITENING LAUNDRY DETERGENTS

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ABSTRACT

The use of microcapsules in home care products as detergents has drawn great attention because of their capacity to improve the properties of the products. In this work it is proposed an encapsulation method of the blue dye. By encapsulating the dye, the intense dark blue color of the detergent will be notably decreased or inexistent making the appearance of the solution cleaner and safer to the consumer's eye. Hence, these detergents can expand and increase their market that now is dominated by fluorescent whitening agents (FWA), which have the same purpose but are considerably more expensive. Since these microcapsules would be produced at an industrial scale, it is important for them to be biodegradable and have a simple production process. A mixture of calcium alginate and polyethylene glycol dimethacrylate (PEGDMA) is proposed as shell materials of the core-shell microcapsules. To produce the microspheres, it is proposed to spray the core-shell plus dye mixture into a cross-linking medium. As an encapsulation process, it is proposed a complexation of alginate and photopolymerization of PEGDMA to harden the shell structure. FTIR analysis of the microcapsules can be done to follow the cross-linking reaction.

1. Introduction

In textile industry, to reach a high degree of whiteness is not difficult to achieve. There are several methods, for example the use of bleaching agents such as chlorine or hydrogen peroxide. These agents whiten or lighten the textile by solubilizing the substances that give color through oxidation or reduction reactions. However, the task to maintain the brightness and the intense white color can be a problem; the textile usually tends to get dull or yellowish and can get damaged with time after bleaching, even when maintaining a proper washing routine. For this reason, in the 19th century scientists started to search for a solution and began to use bluing agents when washing white textiles [1]. These agents are blue dyes such as ultramarine or Prussian blue. They contain naturally blue pigments that improve the white tone by adding some blue traces on the textile. Since the moment these bluing agents appeared until now, they have been widely used all over the world. However, in the last years new types of whitening products appeared as optical brighteners. Optical brighteners, also known as fluorescent whitening agents (FWA), are chemical compounds that absorb in the ultraviolet and violet region and emit in the blue

region [2]. They have a similar function as bluing agents; the main difference is that they are colorless, which makes the detergent esthetically cleaner to the consumer eye. Because of the intense blue color of detergents with blue dyes, many consumers prefer the colorless whitening detergents. These detergents have a gentler appearance by being colorless, or having a lighter color, appearing to be less damaging to the textile. In fact, both types of products create the whitening impression by dying the textile with substances that emit in the blue or purple region [1]. However, FWA are chemical compounds that are more difficult to produce than bluing dyes, which makes the final product more expensive.

With the aim to solve the problem, encapsulation of blue dye is proposed to change the appearance of the laundry detergent by making it appear cleaner and safer to use. On the one hand, the microcapsules have to be resistant enough to hold the dye inside. But on the other hand, they have to be able to break by mechanical force while the laundry is being washed to release the dye. To date, there are no records of the encapsulation of this dye for this purpose, but there are other substances that have been encapsulated in detergents such as perfumes [3-5]. The most used substances to make microcapsules for laundry detergents are formaldehyde-based compounds like urea-formaldehyde or melamine-formaldehyde [6-9]. However, these materials are not biodegradable since they are highly cross-linked. Also, there are important safety and health concerns about these materials which make them difficult to produce and dangerous to work with. Formaldehyde is known for being a human carcinogenic, a pollutant in indoor spaces and causes a negative impact when released in the environment [10-13]. For this reason, companies started to study new options to use and change the current materials for safer ones [14]. Over the last few years, the use of biodegradable and more sustainable materials for microcapsules has become a need. Microcapsules are not only used in the textile industry but in many other sectors to enhance the functional properties of many products. For example, in the pharmaceutical sector microcapsules are used to encapsulate drugs [15], in food products for additives or flavour encapsulation [16] and in consumer care products to encapsulate essential oils [17]. Recently, it was published that the microcapsule market is projected to be valued at USD 11.8 billion by 2023; compared to 2018, when the estimated value was USD 6.3 billion, a considerable increase is observed [18]. Because the microcapsule industry is growing and the demand of more economical and eco-friendly materials is increasing, a strong innovation in this area is needed.

Hydrogels are 3D networks of cross-linked hydrophilic polymers, and some of them like alginate, polyethylene glycol (PEG) or chitosan are well known for their biodegradable and biocompatible properties [19-21]. Depending on the monomers or mixture of polymers used, their concentration, polymerization and cross-linking method, amongst other reaction conditions, their chemical and mechanical properties can be changed [22][23]. Moreover, these materials are relatively inexpensive because they can be found in nature or be fabricated with simple and inexpensive processes [24][25].
The most used hydrogel in encapsulation technology is alginate [26-28]. Alginate has been widely used in the medical and food industry as a gelling and thickener agent, for dentures impression and wound dressing for its biocompatibility and anti-inflammatory properties [29]. However, alginate, depending on its form, can be a

very porous material which would make the microcapsules ineffective for our purpose [30][31]. A solution to make the alginate microcapsules more stable and compact could be to fabricate shells containing a blend of different polymers; hence, allowing to create a less permeable capsule shell. Possible materials that could be used are acrylic and polyethylene glycol (PEG) derivatives because of their mechanical and chemical properties. However, not all polymers are suitable for this purpose since they need to be compatible with the alginate and dye. For example, some important traits to take into account are: the solubility, biodegradability and economical aspects.

The aim of this study is to propose a method to camouflage the intense color of laundry detergents containing bluing dye by its encapsulation. Herein, the shell material is proposed to be a mixture of Ca-alginate and polyethylene glycol dimethacrylate (PEGDMA). As for the fabrication of the microcapsules, it is proposed to use a spraying method to fasten the process since it is more industrially viable.

2. Encapsulation methods

An encapsulation technique is considered to be a process in which a core material is coated with a wall matrix. The capsules can have different purposes such as: isolation, controlled release of substances or protection from external conditions. The core can be any substance in solid, liquid or gaseous state. Also, it can be a pure material or a mixture of different substances [32].
There are many types of encapsulation techniques and, depending on the materials used, there are important characteristics to take into account before choosing the methodology and all the reaction parameters. When selecting the wall and core materials, a deep study about their compatibility and affinity has to be done. Other parameters like the biodegradability, hydrophobicity, and their physical and chemical resistance have to be considered. After all the relevant parameters are chosen, it is also important to analyze the production costs of the encapsulation techniques and to choose the one which is more compatible with the desired final product [33].

In the recent years, many different encapsulation methods have been developed and new manufacturing techniques have been used as fluidized bed coating [34], freeze-drying [35] or supercritical carbon dioxide systems [36][37]. Thanks to the diversity of methodologies, important characteristics like size, shape and structure can be changed easily. The main morphologies of the capsules are: mononuclear, where a single core is surrounded by a wall material; polynuclear, where more than one core is present in the same capsule; and matrix, where the wall of the capsule is not defined and there is a dispersion of multiple cores in a matrix [38], as seen in Figure 1.

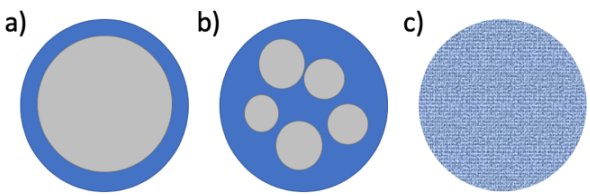

Figure 1. Schematic structure of (a) mononuclear, (b) polynuclear and (c) matrix type capsules.

Once the capsules are formed, it is important to verify their stability and quality. Depending on the encapsulation process their characteristics may vary. One of the most important parameters is the

efficiency of the capsule; it determines the ability of the wall material to contain and hold the core material inside [39]. Other parameters like particle size, homogeneity, and solubility of the capsules have to be considered.

The most common reported techniques to fabricate microcapsules involving water-soluble materials are: spray drying, extrusion and gelation [40][41].

2.1 Spray drying

Spray drying is a very used technique because of its characteristics: it has a flexible process and it is able to work in continuous operation, it makes good quality products and it is economical [42]. It is also a relatively simple method; its steps are basically to prepare a dispersion, homogenize the wall and core materials, atomization of the infeed dispersion and dehydration of the atomized particles. It is a good technique to use with water-soluble materials because at the beginning of the process they need to be hydrated. The average size of the spherical particles can be lower than 100 μm [40][41]. However, the size can be tuned by solely changing parameters like the type of nozzle, feed, air flow rate and temperature [43][44].

2.2 Extrusion

This encapsulation technique is very simple and can vary its methodology depending on the materials used. For example, one of the most used methods is to encapsulate the core material by dispersing and mixing it into the shell material, and then extrude the mixture into a bath with a cross-linker. This method is commonly used with hydrogels like alginate, where the mixed solution is extruded into a gelling bath with calcium ions as cross-linkers [45][46]. Another technique based on extrusion is centrifugal extrusion; it consists in a coextrusion of both core and shell solutions through a rotating head with concentric nozzles [47].

2.3 Gelation

It is a commonly used technique with materials that cross-link in water solutions like hydrogels. It is widely used due to its relatively low cost and easy set-up, which allows to fabricate microcapsules with diameters smaller than 100 μm. This process basically consists in two steps: the formation of the polymer droplets (through a needle or similar setup) and the hardening of these droplets [48].
This technique can be classified depending on the type of gelation employed: external or internal [49], as seen in Figure 2. If an

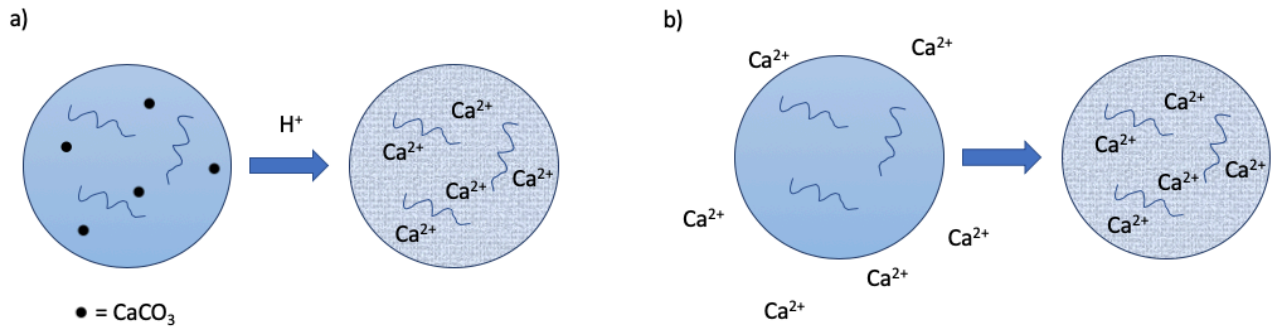

Figure 2. (a) Internal gelation and (b) external gelation of alginate microspheres.

external gelation is produced, it means that the outer layer of the capsule will be harder than the core material. It happens when the shell material is dropped into a solution with the cross-linker and the gelation occurs externally. When the gelation is internal, it means that the polymer solution already has the cross-linking agent, and by activating this agent, for example using an acid to release the calcium ions, the gelation of the whole capsule is done. This may implicate that the microencapsulation efficiency can vary from one type of gelation to another, changing the particle size or homogeneity [50].

3. Shell material analysis

3.1 Acrylic resins

Acrylic resins are materials based on acrylic acid and derivatives. They are well known for their physical and chemical resistance and mechanical strength, which make them very attractive for their many applications. Moreover, the possibility to combine these resins with a wide selection of esters and other monomers with different functional groups makes them very versatile.

There are two types of acrylic materials based on their properties: thermoplastic and thermoset. Thermoplastics can be heated and manipulated in a reversible way. Depending on the polymer or copolymers used, their density, stiffness and toughness can be modified. Acrylic plastics also possess a high weatherability, chemical resistance, thermal and electrical properties and can be biocompatible. They are colorless plastics, which makes them suitable for many medical devices that require a high clarity. On the other hand, thermosetting resins are materials that cannot be manipulated with heat once cured, so they are irreversibly hardened.

Generally, acrylic resins have high chemical resistance to organic solvents and moisture, are stable to UV light and to high temperatures [51]. Their advantage resides in the high variety of properties that they can achieve by only changing and incorporating different monomers into the structure. They are widely used in the medical and health-care industry for their biocompatibility [52—54]; in coatings and adhesives they are used for their weatherability or waterborne properties and for being eco-friendly.

The latest studies about acrylic resins are focused on improving the properties of these materials by adding nanoparticles [52][55][56] or copolymers in the polymerization process. Also, an interest on acrylic-based microcapsules has aroused in many areas for the storage of materials as drugs [57], pigments and phase change materials [58][59]. For example, there are several studies about acrylic-based microcapsules for the self-healing of monuments and cement. Choi et al. [34] developed a new encapsulation method for the control of cement hydration using acrylic resin-based microcapsules (acrylic ester containing acrylamide and acrylonitrile), which had a high physical and chemical resistance. As the encapsulation method, they used fluidized bed. It consists in a dispersion of a solid through a gas, coating the core material with a liquid solution.

Qiu et al. [60] fabricated microcapsules for phase change energy storage materials with polyurea/acrylic resin shells. They used two different acrylic resins: butyl methacrylate (BMA) and methyl methacrylate (MMA); they observed that BMA based microcapsules were more flexible and had a better heat ability and thermal reliability compared to the ones with MMA. On the other hand, Zhao et al. [61] used acrylic based microcapsules for profile control of low-permeability

reservoirs. They prepared polymeric microspheres made of a mixture of monomers (acrylamide, acrylic acid and methyl methacrylate) and N,N-methylene bis-dialkyl-phosphonate acrylamide (MBA) as a crosslinking agent and azoisobutyronitrile (AIBN) as radical initiator. The resulting capsules had good swelling properties, strong temperature and salt resistance and a stable structure.

Silva et al. [62] encapsulated oxidizers in R180W acrylic resin "Redelease" by spout-fluid bed microencapsulation. They successfully formed individual and homogeneous capsules with structural integrity by creating multiple layers of coatings.

Pigments are also substances commonly encapsulated for their release, improving color-related problems. In toners for example, they are used for uniformity problems and to avoid components aggregation or leakage. Ding et al. [58] used a styrene-butyl acrylate to encapsulate pigment PY17 by a mini-emulsion polymerization. The core and shell materials were mixed forming an oil phase and were added dropwise to an aqueous phase to create the mini-emulsion droplets with a size of 80-90 nm. Moreover, microcapsules can be used for textiles and fabrics printing. Haroun et al. [63] used a citric-acrylate oligomer to encapsulate a phthalocyanine pigment using a phase separation method.

Phase change materials (PCM) incorporation in textiles is also an interesting option; it is a suitable method for the laboratory scale production as for the industrial large scale one [59]. PCMs are substances capable of changing their phase from liquid to solid at ambient temperatures. They are a perfect substance to add to textiles since they can regulate body temperature when it is very hot or cold. However, these materials cannot be incorporated directly to the textile so they have to be highly protected, which can be achieved by different encapsulation methods [59][64][65]; using an acrylic resin as the shell material is a good option since they are very resistant as mentioned before. Carreira et al. [66] encapsulated octadecane as a PCM in acrylic based microcapsules via suspension polymerization. They used three different initiators: Benzoyl peroxide (BPO), azobisisobutyronitrile (AIBN) and Trigonox 23 (TRIG) (capable of working at temperatures as low as 40 ºC). For the suspension polymerization, they prepared a solution with all the monomers' mixture, cross-linkers, initiator and PCM and added it dropwise into another solution with water. They obtained well defined core/shell structure microcapsules.

Acrylic resins can be a good material for the encapsulation of the blue dye, but the production costs can be too expensive depending on the resin used. Moreover, there are not many water-soluble acrylic monomers. Also, the capsules have to be biodegradable but in a relatively long-term period, since they should bear the detergent conditions for at least some months, which is essential for our purpose. A solution can be to use a derivative that is resistant enough but also biodegradable.

3.2 Alginate

Alginate is a salt of alginic acid, which is an anionic polysaccharide found in nature (in brown seaweed). Alginic acid is a linear co-polymer formed by D-mannuronic and L-guluronic acid monomers, containing homogeneous blocks of these uronic acids (M, G or MG blocks) as seen in Figure 3. The ratio between the two monomers varies with the source [21]. It is demonstrated that higher ratios of G-units increase the stability of the material; hence, its glass transition (T_g) is increased [67].

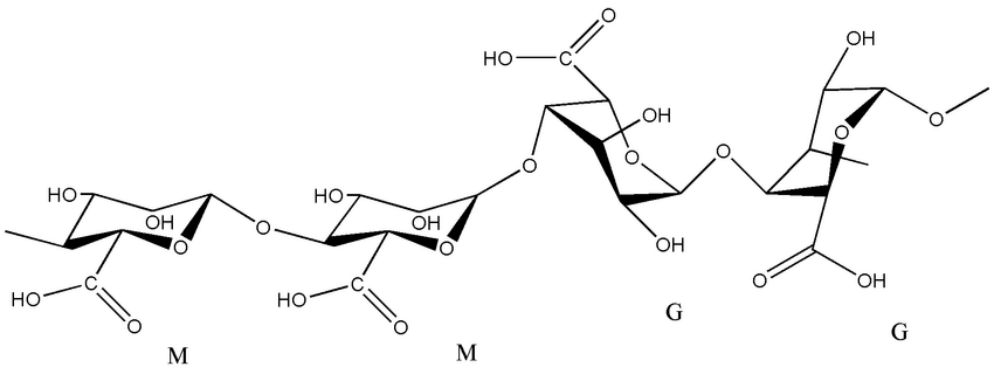

Figure 3. Alginic acid formed of M and G blocks of uronic acids.

Usually, the crosslinking of alginate by ionic bonding uses calcium or sodium. The main difference between using a monovalent and a divalent ion is that with the monovalent ones a low viscosity solution is formed, and with the divalent ones the structure is more compact and forms a gel [68]; divalent ions approach alginate chains via ionic interactions, forming a structure known as "egg box" as seen in Figure 4. Other ions with higher affinity to form the complex can be used such as Cd^{2+}, Ba^{2+} or Cu^{2+} [69]. However, calcium is the most commonly used ion for economical and toxicity reasons.

Alginates have their main applications in medicine and pharmaceutical areas. Because of its biocompatibility, nontoxicity and relatively low cost, this material is used both inside and outside the body [70]. It is commonly used for dentures and wound dressings thanks to its soft gelled form. Also, alginate is widely used to make microcapsules in drug delivery systems [71] and even for personal consumption to improve health related issues like obesity and diabetes [72].

The exchange of ions from sodium to calcium is very fast. Normally, when calcium-alginate is wanted, sodium-alginate is added to a solution of $CaCl_2$. Other sources of calcium can be used as calcium sulfate [73]. In previous works where Ca-alginate was prepared, the concentration of the $CaCl_2$ solution varied depending on the desired hardness of the final material. The role of these cationic ions is to interact with the anionic parts of alginate molecules and cross-link the structure making it harder. To achieve a less viscous and more stable material, normally the concentration of calcium ions is increased; it can also be achieved by controlling the gelation time (from some minutes to hours).

Németh et al. [74] prepared microcapsules using an initial solution of 8% (w/v) $CaCl_2$ and after 30 min of gelation they also used another higher concentration to provide excess of Ca^{2+}. Li et al. [75] used a solution of 1% (w/v) $CaCl_2$ for 24 h to form hydrogels of Ca-alginate and Poly(*N*-isopropylacrylamide) NIPAAm composite. Liu, Z. et al. [76] just washed the gel structure with a 1.1% (w/v) $CaCl_2$ solution twice to not obtain a very hard material. In most of the cases, after the gelation process, the final alginate structure is washed with deionized water to eliminate all the non-bonded ions.

Depending on the structure and composition of the microcapsules, some applications studied in the literature are to encapsulate rejuvenators for asphalt [77], natural pigments like anthocyanin [78], living cells for artificial tissue engineering [76] or guava leaf extract as a natural product in medical textiles [79].

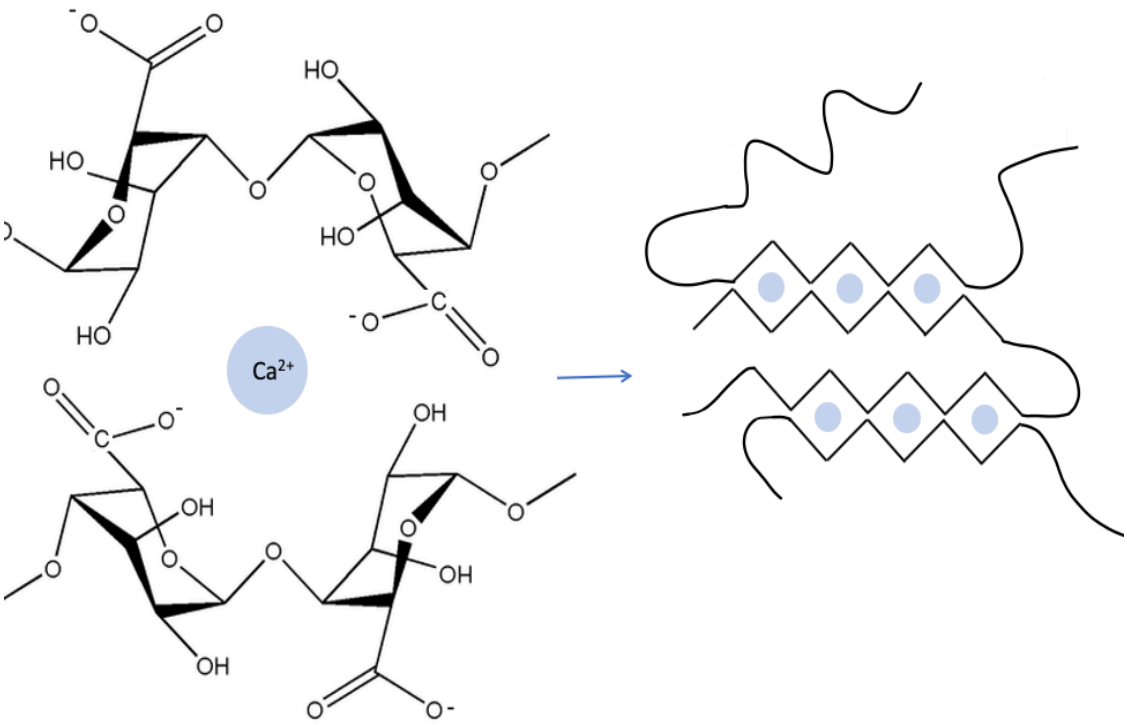

Figure 4. Cross-linking of a divalent ion (calcium) with alginate molecules.

Alginate is a suitable material to use to encapsulate the blue dye for detergents since it is a water-soluble substance, it is inexpensive and biodegradable. However, alginate as a film or in shell capsule form is a porous material. This characteristic would make the microcapsules unable to effectively retain the dye for a relatively long amount of time. On the other hand, as mentioned before, a good characteristic about alginates is that they react very fast, which leads to an instantaneous formation of the capsule; hence, alginate can be used as an outer shell.

3.3 Polyethylene glycol

PEG is a homopolymer of ethylene oxide. It is a flexible water-soluble material, which makes it suitable for many applications like lubricant formulations [80], medical uses such as laxatives [81] or drug carriers [82], and in cosmetics as a basis for skin creams [83] thanks to its biocompatibility [84]. It can be used in many areas thanks to its large structure diversity and molecular weight variability. Moreover, its structure allows to be easily modified with different functional groups, as seen in Figure 5, which can change completely its properties (e.g. viscosity) and application.

This polymer is mostly used at a larger scale for its viscosity and swelling properties. However, it is commonly combined with other polymers to improve its properties and malleability. PEG capsules were fabricated before for different medical purposes like drug delivery [85] or ovarian tissue encapsulation [86]. However, there are not many studies about the fabrication of PEG based microcapsules. Watanabe et al. [87] fabricated (tetra-PEG) hydrogel microcapsules with an aqueous core for drug delivery purposes in medicine and for cell encapsulation.

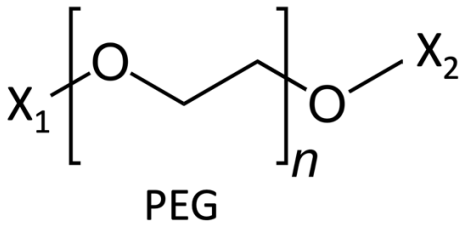

Figure 5. Common structure of linear PEGs, where X are functional groups, e.g. NHS or COOH.

A possible way to successfully make PEG or PEG derivatives based microcapsules could be mixing this polymer with other polymers (e.g. alginate) for a more stable and resistant structure by combining their mechanical properties. Shapiro et al. [88] fabricated a composite hydrogel with PEGDMA and calcium alginate to mimic soft tissues for biological applications; they obtained a compact and stable material.

The best way to fabricate PEG hydrogels is by free radical polymerization; it has high reaction rates at room temperature, it needs low energy inputs and for its chemical versatility [88-90]. There are reported many reactions of PEG derivatives undergoing free radical polymerization. Mostly, they are combinations of acrylate, methacrylate or dimethacrylate end of chain groups [91][92], although other groups like nitrocinnamate have been used [93].

Several photopolymerization processes were described using PEG derivatives. Burke et al. [94] used Irgacure 2959 (Darocur 2959) for PEGDMA and tried two different UV sources (UV chamber Dr. Gröbel UV-Electronik GmbH and UV handheld lamp (B-100AP/R)) and compared the duration of cure of each method; Burdick et al. [95] also used this photoinitiator for PEGDA cross-linking to fabricate hydrogel disks. From the same series, Irgacure 184 was used as photoinitiator for a mixture of polyethylene glycol methacrylate (PEGMA) and PEGDMA [96]. Tucker et al. [97] used 2,2-dimethoxy-2-phenylacetophenone (DMPA) as the photoinitiator for PEGDMA in a UV-box (UVITEC, CL508-BL, UK) to form hydrogel tablets.

In the other hand, catalysts like catalase [98] or horseradish peroxidase and hydrogen peroxide (H2O2-HRP) [99] were also used for the polymerization of PEGDA and PEGDMA respectively. Another option is to use initiators such as azobisisobutyronitrile (AIBN) [100] or Ammonium persulfate (APS) [88].

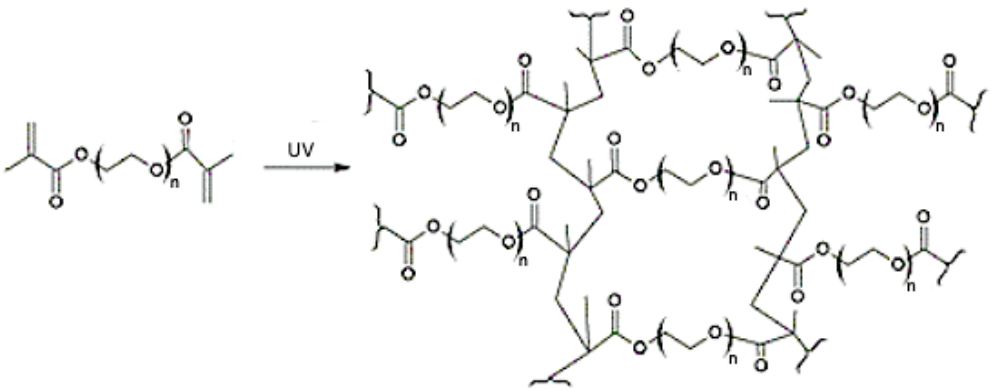

Figure 6. Cross-linking of PEGDMA by photopolymerization

PEG derivatives as PEGDMA can be a good shell material to be combined with alginate since they are compatible and are both water-soluble and biodegradable. PEGDMA could not be used as the only shell material for the encapsulation of the dye because the formation of the microcapsules would be too laborious; its polymerization is not fast enough to make the capsule structure right after the creation of the droplet, as it is possible with alginate.

4. Experimental proposal

After analyzing different encapsulation methods and the possible materials of the core/shell structure, it is proposed to use Ca-alginate and PEGDMA as the shell materials. The main characteristics of these polymers that make them suitable for this research are their compatibility and good chemical and mechanical properties. Both polymers are water-soluble, which makes them the perfect candidates for the encapsulation of water-soluble materials as is the blue dye. Moreover, alginate is well known for its biocompatibility and malleability [101]. PEGDMA has combined properties of PEG and acrylates, making it a convenient material for the shell since it has good thermal and mechanical properties and it is also known for being biocompatible [102].
For this reason, the mixture of these materials would make a suitable microcapsule for our purpose; alginate, even if it is porous, can cross-link and form an outer shell very fast, while PEGDMA polymerizes slower but it is able to make a resistant and more compact inner shell, thanks to its cross-linking as seen in Figure 6.

As reported previously, there are several encapsulation methods that were used with these polymers, but one of the most simple and viable one is by external gelation of alginate and photopolymerization of PEGDMA. To create many microcapsules at a time, the mixture with the core, shell materials and photoinitiator can be sprayed into a cross-linking medium, as seen in Figure 7. In this way, the microcapsules with the core material inside are formed instantly. Hence, all the materials used have to be water soluble since the reaction is made in water medium.

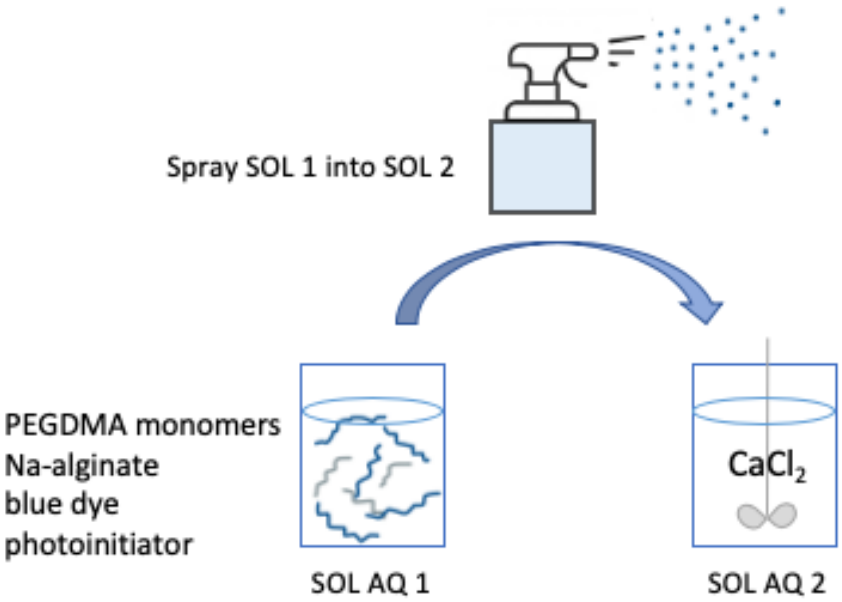

Figure 7. Schematic representation of the encapsulation process.

4.1 Materials and conditions

All the following reagents are available in Sigma-Aldrich.
To prepare Ca-alginate microcapsules, it is needed to first cross-link Na-alginate with calcium. For this reason, a solution with Na-alginate and another with $CaCl_2$ are needed. Depending on the concentration and time of reaction of calcium ions with sodium alginate, the molecular weight of alginate can vary significantly and improve the physical properties of the gel. However, a very high molecular weight is not desirable because of its extreme viscosity [103]. Hence, the concentration of $CaCl_2$ and reaction time has to be optimized. Moreover, the pH also affects the viscosity of alginate gel; the viscosity of the solution increases with lower pH because more hydrogen bonds are formed [101]. An initial concentration of 1% (w/v) $CaCl_2$ at neutral pH is proposed since several experiments were successfully done with similar conditions [75][103][104].

It is proposed to use PEGDMA with a molecular weight between 250 and 500. Higher molecular weights would increase considerably the swelling capacity of the hydrogel [105], which is not desirable for the microcapsules. The most suitable process to cross-link PEG hydrogels is by free radical polymerization. Photo-polymerization is a good option since it is a simple and fast process. Hence, a water-soluble photoinitiator is proposed to use; Irgacure 2959 has been reported to be effective for the photopolymerization of PEGDMA [94][102][106]. Arcaute et al. [106] observed that at high concentrations this photoinitiator loses its water solubility, which makes its use viable only at low concentrations.

The effect of the irradiation intensity of the UV light and time of exposure have to be optimized. Killon et al. [102] used a UV curing chamber with 20-UV tubes with a spectral range between 315-400 nm and an intensity of 10–13.5 mW/cm^2 during 10 min. Whereas Burke et al. [94] used a UV lamp at an intensity of 100 W with a 5 cm aperture and an average intensity of 21.7 mW/cm^2. After 10 min they observed the lowest swelling degree and the maximum at 25 min.

To create the droplets, it is proposed to spray the solution 1 (with all the microcapsule materials) into the solution 2 (with the cross-linking medium for alginate), as seen in Figure 7. However, at the lab scale it can also be used needles to make them.

4.2 Methodology

In this work it is proposed a simple system where a solution with water-soluble polymers are sprayed into another water solution. Hence, two aqueous solutions are needed. One is made of a homogeneous mixture of PEGDMA monomers, Na-alginate, the blue dye and the photoinitiator (Irgacure 2959). The second solution has a concentration of 1% (w/v) $CaCl_2$ as a source of calcium; hence, the water solution used has to be deionized water to have a proper control of the concentration of calcium ions. While the polymer mixture is sprayed into the second solution, this has to be gently stirring to form the microcapsules and to ensure a homogeneous cross-linking of alginate. To ensure the complete complexation of alginate with calcium ions, the solution can be left to react up to 4h, since it has been reported to be enough time to complete the ion exchange of sodium to calcium [30]. After Ca-alginate is formed, it is needed to activate the photoinitiator and start the photo-polymerization reaction of

PEGDMA. It can be used a UV lamp (Helios Italquartz) with a spectral range between 400-100 nm. To obtain the capsules it is needed a filtration; the capsules have to be washed with distilled water.

4.2. Characterization

To know when the capsules are completely formed, a FTIR scan can be done to follow the exchange of Na to Ca ions. As shown in Figure 8, sodium alginate has an absorption band at 2920 cm^{-1} (C–H stretching). In Ca-alginate spectra, this band cannot be seen since the stretching of C–H is more limited because of the complexation with the divalent ion. Also, in Ca-alginate spectra it can be observed the stretching vibration absorption band of C–O at 1074 cm^{-1}; this band is weaker for Na-alginate [107].

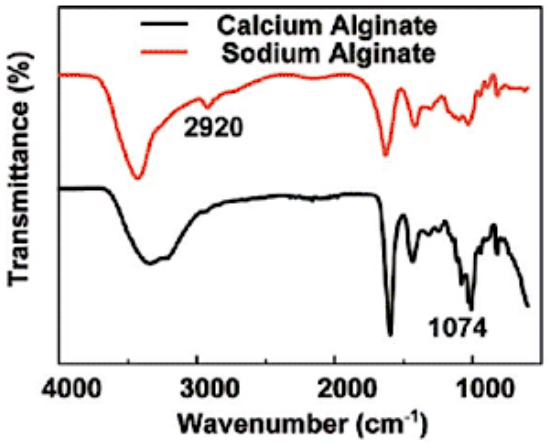

Figure 8. FTIR spectra of Ca-alginate and Na-alginate [107].

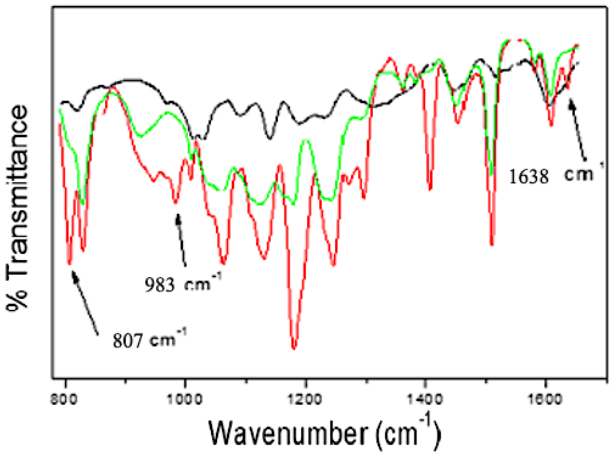

Figure 9. FTIR spectra of an acrylic resin (ET10) before UV-curing (red line) and after curing (green line) [109].

To follow the cross-linking reaction of PEGDMA, spectroscopy measurements on the obtained microcapsules can also be done. With a FTIR scan it can be observed the characteristic peaks of acrylic resins: 1638 cm^{-1} (acrylic C=C stretching), 983 cm^{-1} and at 807 cm^{-1} (=C–H stretching). When all the monomers have cross-linked, these acrylate peaks will be strongly or completely reduced, indicating the end of the reaction [108-110], as seen in Figure 9.

5. Discussion

In this study it is evaluated a method to prepare microcapsules using PEGDMA and Ca-alginate for the encapsulation of water-soluble dyes. Using these polymers to make the microcapsules is a good eco-friendly alternative to the currently used ones since they are biodegradable. Moreover, a simple method to fabricate the microcapsules is exposed only requiring two basic steps: first the cross-linking of alginate, and secondly the hardening of the shell structure by the photo-polymerization of PEGDMA monomers. With these microcapsules, the dye inside is well protected from leakages from the beginning; Ca-alginate forms rapidly the capsule structure and PEGDMA hardens the capsule from inside.

The detergent containing the encapsulated dye can be more aesthetic for the consumer since the solution has a cleaner appearance. Hence, it can be concluded that by

encapsulating the dye, the consumer can have a better experience with the product. Additionally, since the microcapsules employed are biodegradable and fabricated by a simple process, they are suitable for industrial production.

Keywords

Microcapsule, biodegradable, hydrogel, laundry detergent.

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