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BIODEGRADABLE DYE ENCAPSULATION USING ALGINATE AND POLY(ETHYLENE GLYCOL) DIMETHACRYLATE

MASTER'S DEGREE THESIS

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Abstract: Encapsulation technology have led to the evolution of many sectors since it can control some properties or change some functions of the final product. In this work, a dye is encapsulated using alginate and polyethylene glycol dimethacrylate (PEGDMA). 3 types of shell materials were studied: alginate alone, alginate with PEGDMA irradiated directly (at 0h) with ultraviolet (UV) irradiation to start the polymerization of PEGDMA, and alginate with PEGDMA irradiated after 24 h. These three types of capsules were characterized to compare the different properties. The optical microscope was used to measure the average diameter of the capsules, the scanning electron microscope showed that capsules made of both monomers containing the dye and irradiated directly had an empty core and a heterogeneous structure while those irradiated after 24h had a more homogeneous morphology. The fourier transform infra-red (FTIR) was used to prove that the chemical reactions of alginate crosslinking and PEGDMA polymerization occured. Mechanical analysis of the capsules showed that alginate capsules were stiffer and the incorporation of PEGDMA showed a different rupture mechanism like an exfoliation instead of a crush for capsules irradiated at 0h. The Total organic carbon (TOC) and biological oxygen demand (BOD) tests were done on solutions containing dissolved capsules and showed that the presence of the PEGDMA monomer didn't affect the water quality. Also, thermogravimetric analysis (TGA) was done on the capsules to check the quantity of the calcium ions present and the FESEM to check its distribution, this showed that the capsules irradiated directly probably trapped calcium and didn't allow it to crosslink the alginate chains while the presence of the dye didn't have any significant effect on the calcium concentration.

Introduction

Bleaching agents are one of the most important ingredients of the laundry detergents. These agents are mostly chemical, and they consist either of chlorides, hypochlorites, or peroxides that can clean the clothes and remove the dirt, grease, and soil through the oxidation and the reduction reactions they undergo. This action can lead to cleaning the clothes temporarily; however, on a longer timescale it leads to another problem which is the yellowing of the white-colored clothes and their damage over time[1]. So, this presented a challenge for the laundry detergents industry and to solve this problem, they used several additives.

The first additive that appeared in market was the bluing agent that was out in the middle nineteenth century. The bluing agents were able to solve the yellowing problem due to their blue color which counteracts with the yellow color formed on the clothes to give an increased sense of whiteness. However, this also posed a problem since consumers didn't like blue-colored detergents and preferred colorless or white ones as they appear "cleaner".

For this reason, in modern detergents, another additive is added which is the fluorescent whitening agent (FWA). They were able to achieve the same effect of the bluing agents while working with a different mechanism and having a different color. FWA are organic compounds, and as their name says they are fluorescent, so they can absorb in the ultraviolet region

and emit in the visible blue region[1,2]. Clothes having a yellow color are able to reflect all colors and absorb the blue color. So, FWAs can compensate this blue deficiency and make the clothes appear whiter and brighter. On the other hand, at an industrial scale FWAs are hard to be made and processed, so this will increase the final cost of the detergent.

That being the case, we are proposing the encapsulation of the blue dye to decrease the intensity of the blue color in the detergent while maintaining its low cost at the same time. Encapsulation is generally referred to covering a core material, which can be either a solid, a liquid, or a gas, with a shell. It can protect the inner material from harsh environment outside, resulting in maintaining its important characteristics for a longer time and preventing undesired interactions, or control the release of this material under specific conditions and in desired positions[3].

Different microencapsulation methods have been utilized according to the shell material to be used. This technology has been used in several industries to provide new properties and enhance already present ones. For example, in the food industry it has been used to control the release of some additives or mask some undesired flavours[4]. In the pharmaceutical industry, it was also used to encapsulate some drugs to control their release and target tumour sites[5]. Moreover, this was also present in the cosmetics sector where some oils can be encapsulated to preserve them in a fresh way for a longer time[6].

Moving to the laundry detergent industry, microencapsulation was used before for encapsulating fragrances. This preserves the perfumes for a longer time through protecting them from the detergent media and controlling their release while or after washing using polyurethane/urea microcapsules[7] or polysulfone microcapsules[8]. However, due to the detergent's aggressive media the only capsule material that was successful industrially was that based on formaldehyde material like urea formaldehyde and melamine formaldehyde[9–11]. This type of material is not biodegradable and there are some concerns about its effect on the health and on the environment like being carcinogenic or being considered as an indoor pollutant[12–14]. On the other hand, there are no previous records for the encapsulation of the blue dye in the detergent industry.

Hydrogels are materials that can crosslink and form a gel and they are usually used as shell materials. Shell materials are chosen according to the application and the respective properties needed. In this case, we proposed a mixture of sodium alginate and polyethylene glycol functionalized with acrylate to be used. Alginate is a family of polysaccharides that are extracted from algae and treated to form sodium alginate; so, they are biodegradable, nontoxic, and most importantly they can form a gel. Gel formation is allowed in the presence of divalent cations such as calcium in calcium chloride that can act as crosslinks between the functional groups of different chains of alginate[15] (Figure 1.b). On the other hand, polyethylene

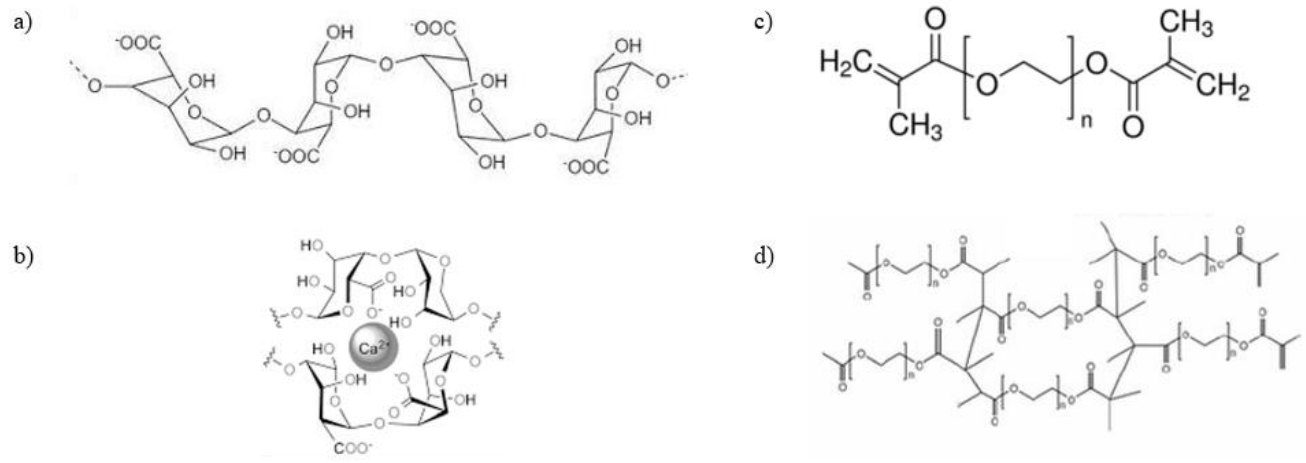

Figure 1: a) Chemical structure of alginate chain b) Crosslinking of alginate chains by calcium ions, c) Chemical structure of PEGDMA, d) Photopolymerization of PEGDMA

glycol is a homopolymer of ethylene oxide that is also biocompatible, and when functionalized with acrylates, can form a gel through free radical polymerization in the presence of an initiator (Figure 1.d).

Alginate can form the initial capsule shape through crosslinking; then, the polymerization of the poly(ethylene) glycol dimethacrylate (PEGDMA) under UV light will take place, and it is expected to increase the stability of the shell[16]; so, the capsule will be able to hold the dye stable in the detergent media and release it after its mechanical breakage in the washing machine. The incorporation of two components in the shell material is expected to provide versatility in the different properties.[17,18] That is why the alginate capsules will be compared to the multicomponent capsule to study various characteristics. Therefore, we are providing a new method for encapsulating dyes respecting the biodegradability aspect, which is important at the industrial scale for large production.

Experimental Section

Chemicals and Materials:

Sodium Alginate A3249,1000 (Lot: 9N013872) was purchased from Panreac ITW Reagents. Calcium Chloride (Lot: J2390) was purchased from Honeywell International Inc. Auramine O Dye, Dye content>80% (Lot: SHBL5991) and Reactive Orange 16, Dye content>70% (Lot: MKCG2976) were purchased from Sigma-Aldrich. Dye X was used but no information was provided about it.Poly(ethylene Glycol) Diacrylate (PEGDA) (Lot: MKCL7365), 2-Hydroxy-4´-(2-Hydroxyethoxy)-2-methylpropiophenone, 98% (Lot: MKCM0581), and 2-Hydroxy-2-methylpropiphenone, 97% (Lot: MKCJ2148) were purchased from Sigma Aldrich. Poly(ethylene)glycol 400 Dimethacrylate (PEGDMA) was purchased from SARTOMER. All chemicals and reagents were used as provided without any further purification.

Preparation of Macrocapsules:

To study the effect of different conditions different types of capsules were prepared. the different polymeric solutions used are summarized in table1. In each case, the polymeric solution is taken, mixed to have a homogeneous state, and then it is extruded through a syringe-needle system to be added to the crosslinking solution, which is the calcium chloride solution, in forms of drops. The pump used for the extrusion of the polymeric solution is used at a flowrate of 1 ml/min and considering the distance between the needle and the crosslinking solution as 5.5cm. Once the droplets reach the solution the alginate chains start crosslinking to form the initial capsule shape. The crosslinking solution consist in all cases of 2%w/w calcium chloride.

In the cases where there are two monomers involved in the shell material, the second monomer which is either PEGDA or PEGDMA must be polymerized through UV exposure. This exposure is in all cases done using the UV curing lamp from Helios Italquartz and it is done for 5 mins using 50% power at 7.5A. The time of the UV irradiation is varied between capsules, where some capsules are irradiated directly after being extruded into the crosslinking solution and then left on stirring for 24 hours, while others are stirred for 24 hours and then irradiated. After that the capsules are filtered and put in the oven at a temperature of 40°C for 24 hours after which the capsules are collected.

To choose the photoinitiator to be used, two solutions were prepared one containing 1g of PEGDA and 0.05 of 2-Hydroxy-4´-(2-Hydroxyethoxy)-2-methylpropiophenone and the other containing 1 g of PEGDA and 0.05g of 2-Hydroxy-2-methylpropiophenone. Few drops of these two solutions were left in ambient light and few drops were put in the oven at 40°C. Then, their performance was tested under UV light. Both photoinitiators worked only under UV light so they were suitable for the application. The photoinitiator which was used for all the capsules and which is referred to in table 1 was 2-Hydroxy-2-methylpropiphenone since it was more soluble with the monomer. This photoinitiator was also tested with the different reactants like the alginate and the dye to make sure it was not giving any undesirable effect.

Table 1: Different Polymeric Combinations used for capsules formation

Sample	Alginate (%w/w)	PEGDA (%w/w)	PEGDMA (%w/w)	Photo initiator (%w/w of monomer2)	Dye(%w/w)		time of UV Irradiation (h)
1	1	-	-	-	-	-	-
2	1	-	-	-	Reactive Orange 16	1	-
3	1	-	-	-	Reactive Orange 16	0.1	-
4	1	-	-	-	Reactive Orange 16	0.2	-
5	1	-	-	-	Reactive Orange 16	0.3	-
6	1	-	-	-	Auramine O	0.03	-
7	1	-	-	-	Dye x	0.1	-
8	1	-	-	-	Dye x	0.3	-
9	1	-	-	-	Dye x	0.5	-
10	1	-	-	-	Dye x	0.8	-
11	1	-	-	-	Dye x	0.8	0
12	1	1	-	5	Dye x	0.8	0
13	1	1	-	5	Dye x	0.8	24
14	1	-	1	5	-	-	0
15	1	-	1	5	-	-	24
16	1	-	1	5	Dye x	0.8	0
17	1	-	1	5	Dye x	0.8	24

Characterization of the Macrocapsules:

1. Optical Microscope

The capsules were observed under the Leica DMS 1000 optical microscope. Then through the imageJ software an average diameter of each sample of the capsules is calculated.

2. Environmental Scanning Electron Microscope (ESEM)

Six samples were taken to observe their morphology through the environmental scanning electron microscope ESEM FEI Quanta200. First the capsules were put on a tape surface and the samples were coated with gold using the quorum Q150TS Plus. Then the samples were transferred to the ESEM which was operated at voltage 20kV. The outer surface was observed. Then samples of the capsules were cut into slices to observe the cross sections. This was applied on the samples 1,10,11,14,16,17. The capsules slices were glued on the microscope slide and coated with gold to be observed by the ESEM.

3. Fourier Transform Infra-Red (FT-IR)

To monitor the progress of the chemical reactions which are the crosslinking of alginate by the calcium ions and the polymerization of the acrylate, the Fourier Transform Infra-Red (FTIR) Vertex 70 from Bruker was used. The FTIR spectra were recorded at an average of 16 scans in the range of 300 to 4000 cm^{-1} at the resolution of 4 cm^{-1}.

4. Mechanical Analysis

Dynamic mechanical analysis was carried out using the DMA Q800 V21.3 Build 96 from TA instruments working on a controlled compression force on the

capsule samples. The three samples tested were 10, 16, and 17.

For the alginate-dye sample, 7 capsules were tested, for the alginate-PEGDMA-dye irradiated at 0h 8 capsules were tested, and for the capsules irradiated at 24h 9capsules were tested. The temperature, the position of the probe, the force applied, the stress, the strain, the stiffness, the creep compliance and the relaxation modulus were recorded with respect to the time until the rupture occurs. The maximum force obtained for each capsule is recorded. On the other hand, the stiffness value can be obtained for each capsule by taking the slope of the linear part of the force variation as a function of length.

5. Total Organic Carbon

500mg of capsules of the sample 1,14, and 15 were taken and crushed through a coffee crusher machine for 30 seconds and then put in a 50ml solution of milliQ water and left on the stirrer for 24 hours. After that the solution was filtered, the remaining capsules were dried and weighed, and the solutions were analysed using the TOC-L from Shimadzu equipment. For each sample the experiment was repeated for 3 times.

6. Thermogravimetric Analysis (TGA)

Capsules of the samples 1, 10, 14, 15, 16, and 17 were tested by the thermogravimetric analysis equipment TGA 2 STARe System from Mettler Toledo. The samples´ behaviour was studied under a nitrogen flowrate of 50 ml/min and a temperature range starting at 30°C and until 600°C with an increase rate of 10°C/min.

Also, solutions used for the TOC were put in the oven dried and the dissolved capsules were recovered and tested at same conditions in the TGA.

7. Biological Oxygen Demand (BOD)

After ensuring that part of the capsules is being dissolved in water, then BOD can be applied as only liquid samples can be tested. According to the average values obtained from the TOC experiments for each kind of capsule and using the relation provided by Dubber et al.[19] the BOD expected values were calculated and according to these values, the expected BOD range was chosen, and the respective sample volume needed was detected. Thus, 3 solutions were prepared the first one contained 3.7g of alginate capsules in 370ml of milliQ water. The other 2 solution contained 1.7g of capsules in 170ml of milliQ water. The solutions were left on the stirrer for 24 h after which the undissolved capsules were filtered, and the solutions were used.

The BOD equipment used was the BOD system AL606 from Aqualytic and the steps provided by the instruction manual were followed. First the pH of the solution was adjusted to be between 6.5 and 7.5 which is the optimal range for BOD measurement. Then 360ml was taken for the solution containing the dissolved alginate capsules and 157ml was taken for the other two solutions and according to these volumes the required amount of the nitrification inhibitor is added to inhibit the nitrification reaction. After that, a stirring rod is added to the bottles and they are sealed tightly by placing the BOD sensors into the bottles´ rack. The system is placed in a thermostatically controlled cabinet at 20°C. Then the measurement process can be started. The sample is incubated for 5 days after which the BOD values can be read.

8. Field Emission Scanning Electron Microscope (FE-SEM)

The FESEM equipment was used on two samples to check capsules made of both monomers containing the dye and irradiated at different times to check the difference in the distribution of the calcium ions in the capsules.

The FESEM-FIB Scios 2 from FEI Company was used. The microscope slides containing cut slices of these two samples of capsules were used. The slides were first coated with carbon due to the high vacuum and the Energy Dispersive X ray Spectroscopy (EDX) was used for analysing the elements distribution in the capsules.

Results and Discussion

Preparation of Macrocapsules:

The first step was to study the solubility of the different dyes present to be able to choose the one that fits our system. The reactive orange 16 and the auramine O dyes were tested, the first one showed a solubility of more than 1%, so after preparing the polymeric solution with alginate and making the capsules it was obvious that the dye was being released directly from the capsules. Even after decreasing the amount of dye, the same problem was encountered. Then the auramine O dye was used for encapsulation with a very small amount (0.03%) due to the limit of its solubility in water. However, the dye was also released from the capsules to the crosslinking solution. The third dye was tried through different concentrations (0.1,0.3,0.5,.0.8%). It showed a good performance it was stable inside the capsules without being released at least for the 24 hours in which the capsules where still in the crosslinking solution before being filtered and dried. The highest successful concentration which was 0.8% was used in all the other upcoming capsules. First the second monomer incorporated in the polymeric solution was the PEGDA it was tried with the photo initiator and showed good polymerization. However, when the capsules were done and after the irradiation of the batch by UV light, the polymerized PEGDA appeared in the solution outside the capsules. So, in this case the PEGDA was directly diffusing outside of the capsules into the calcium chloride solution. For this reason, another type of the monomer was tried which is the PEGDMA, in this case the capsules containing the two monomers could be prepared and the monomer was polymerized while still in the capsule to do its required function.

Characterization of Macrocapsules:

1. Optical Microscope

The average diameters of the different samples prepared are summarized in the table below. It can be observed that there is no big difference in the results as all the conditions like the syringe used, the needle diameter and the polymeric solution flowrate were constant through all the samples.

Table 2: Average Diameters of different types capsules

Sample	Average Diameter (mm)	Sample	Average Diameter (mm)
1	0.648	12	0.691
7	0.624	13	0.697
8	0.641	14	0.736
9	0.675	15	0.75
10	0.657	16	0.625
11	0.732	17	0.694

2. ESEM

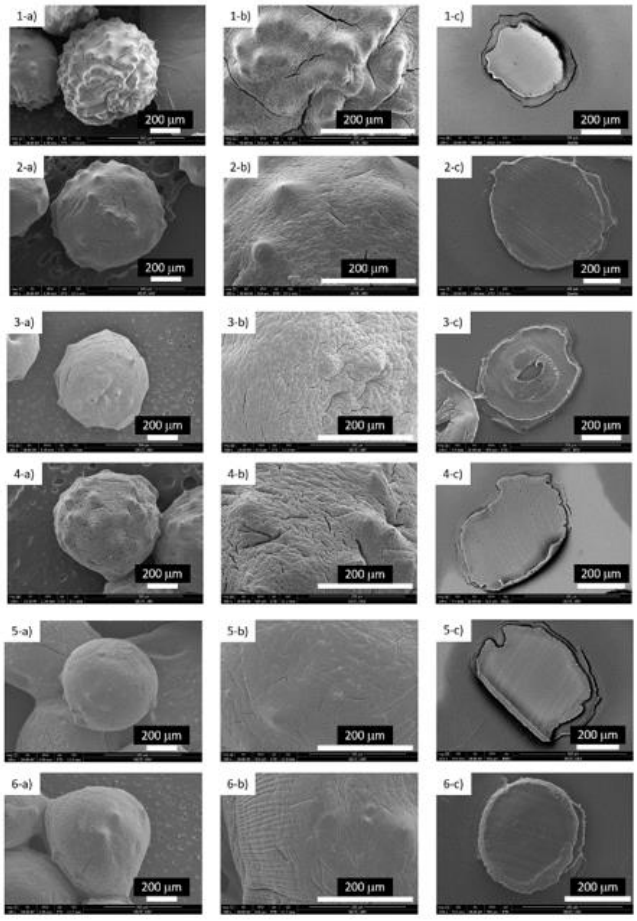

Figure 2: ESEM Photos: a) capsule, b) Surface, c) crossection; 1)alginate-dye capsule, 2)alginate-dye capsule irradiated, 3)alginate-PEGDMA-dye irradiated at 0h, 4)alginate-PEGDMA-dye irradiated at 24h, 5)alginate capsules, 6)alginate-PEGDMA caps

According to the photos obtained by the ESEM, we observed that the alginate with the dye capsule had the roughest surface of all samples (Figure 2.1-a). When this sample is irradiated (Figure 2.2-a), we can see that the outer surface is smoother, but the cross-section remains the same. The sample containing the alginate-PEGDMA-dye which was irradiated directly after being formed showed also a smooth surface (Figure 2.3-a), however the cross-section photo showed a hollow sphere (Figure 2.3-c) where the dye is expected to be in the center and the PEGDMA crosslinks after irradiation without allowing the dye or the calcium ions to diffuse in the capsule. This type of capsule showed a form of two layers in the shell and an empty core. On the other hand, when the capsules were irradiated after 24 hours the cross-section was uniform and homogeneous (Figure 2.4-c) and it appeared that the dye was able to diffuse through the capsule before the PEGDMA was crosslinked after 24 hours although it still contained some very small pores inside it. The capsules formed of the polymers without the dye (Figure 2.5-a, 2.6-a) have a much smoother outer surface. It was also shown that when the 2-monomer capsule didn't contain the dye its crossection was more homogeneous

3. FTIR

The FTIR spectra are displayed in Figure 3. The spectrum of sodium alginate showed different bands. The band at about 1029 cm^{-1} was attributed to the C-O-C stretching. The peaks at 1407 cm^{-1} and 1600 cm^{-1} are due to the carboxylate group ($-COO^-$) symmetric and asymmetric stretching respectively. Finally, the broad peak centred at about 3260 cm^{-1} is due to the -OH stretching. To study the crosslinking of alginate using calcium chloride, the spectra of sodium alginate and that of the alginate capsules were compared. When the capsules are formed, the sodium ions are replaced by the calcium ions which leads to the change in some factors like the radius, the charge density and the atomic weight of the cation which leads to changes in the spectra. These changes appear in the shift of the peak related to the symmetric stretching of the carboxylate group[20]. Also, it is observed that the peak related to the hydroxyl bonding becomes narrower and of higher intensity after crosslinking [21].

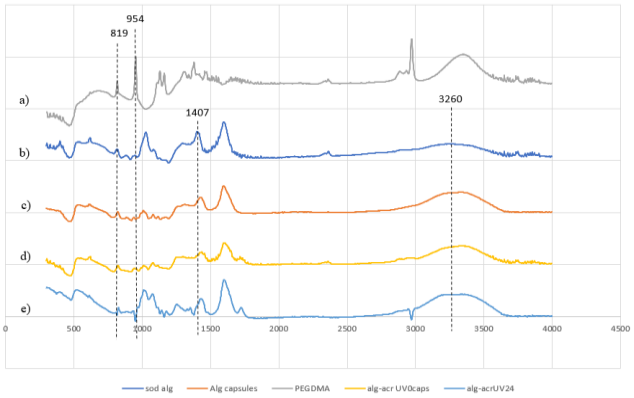

Figure 3: FTIR spectra of a) PEGDMA, b)sodium alginate, c) Alginate capsule, d) alginate-PEGDMA capsule irradiated at 0h, e) alginate-PEGDMA capsule irradiated at 24h

To study the photopolymerization of the PEGDMA also the spectra of PEGDMA monomer was compared to that of the capsules and it was shown that the peak at 819 cm^{-1} decreased corresponding to C=C twisting[22,23] and the peak at 954 cm^{-1} disappeared and it is attributed to C=C bending[24,25]. However, since these peaks were not totally reduced, it appears that the polymerization reaction was not complete.

4. Mechanical Analysis

According to the preliminary mechanical results the samples of the capsules with alginate and the dye only appear to be more resistant as the average maximum force is more having an absolute value of 10.49 N and 19.55 N/mm (when normalized with respect to the diameter) and it is also stiffer having a stiffness of 54.21 N/mm. On the other hand, the capsules containing the two monomers and irradiated at 0h and those irradiated at 24 h had a similar behavior being less brittle with a lower value of the maximum force of 7.68 N (15.44N/mm) and 7.56 N (15.92N/mm) respectively, and a lower value of the stiffness being 38.91 N/mm and 33.74 N/mm respectively. These results are in accordance with literature where alginate is stiffer and the presence of PEG based monomer makes it more flexible.[18]

One observation that was recorded was a great dispersion in the values of the parameters in the sample of the capsules made of the two monomers and irradiated at 0h having a standard deviation of the stiffness value of 25.81N/mm; on the other hand, this

was much less for the capsules taken from the sample irradiated at 24h where the value of the standard deviation was 5.75 N/mm. This difference was attributed to one of the two causes: either the experience gained from the first experiment, so the measurements obtained later were better, or they can also be related to the morphology of the capsules obtained by the ESEM photos, were the capsules irradiated after 24h showed a more homogeneous capsules while the ones irradiated at 0h showed a heterogeneous and nonuniform structure.

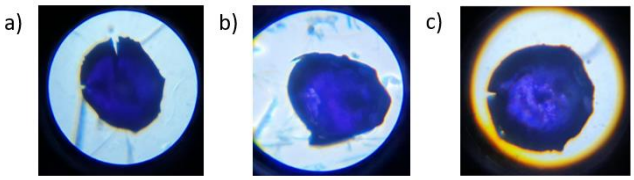

Figure 4: Photos after rupture of a) alginate capsule, b) alginate-PEGDMA-dye irradiated at 0h, c) alginate-PEGDMA-dye irradiated at 24h

Also, we can observe a difference between the three samples according to the breaking mechanism (Figure 4). Where the alginate capsules show a fracture, while the capsules containing the two monomers and irradiated at 0h showed different behaviour like an exfoliation or a peeling behaviour instead of a crack. This was not observed in the capsules irradiated after 24h where a crush is mainly observed. This is also attributed to the internal structure of the capsules where the capsules irradiated at 0h and having a multi-layer cross-section are being exfoliated in form of layers whereas the homogenous capsules are crushed.

5. Total Organic Carbon

It was shown from this that the amount of dissolved capsules made from the two polymers and irradiated at 0h was the highest, which was unexpected as it should be more crosslinked, whereas the capsules irradiated after 24h were the least dissolved. The concentration of the total organic carbon dissolved and analysed in the solutions was much lower for the alginate solution containing dissolved alginate capsules although the mass of the capsules dissolved was comparable. On the other hand, the TOC values of the solutions containing the dissolved capsuled formed of the two monomers were similar despite the difference in dissolution. From this test it was proved that BOD test can be done on the samples and to discuss these results TGA test was done.

Table 3: Dissolution and TOC results of alginate capsules, alginate-PEGDMA irradiated at 0h, and alginate-PEGDMA irradiated at 24h

Sample		500mg capsules in 50 ml water		
		% Remaining	% Dissolved	TOC (mg/l)
Alginate capsules	1	55.3	44.7	35.47
	2	54.06	45.94	35.29
	3	53.88	46.12	20.73
Alginate-PEGDMA (UV0h)	1	42.48	57.52	299.3
	2	46.56	53.44	272.2
	3	43	57	275.7
Alginate-PEGDMA (UV24h)	1	57.34	42.66	274.6
	2	58.86	41.14	261.1
	3	56.88	43.12	278

6. Thermogravimetric Analysis

The curves obtained from the TGA and especially the remaining % weight of the capsules corresponded to the amount of calcium in the samples[26–28]. It was shown that the amount of calcium in the alginate capsules was higher in both cases: without the dye (44.92%w residue) and with the dye (44.34%), while in the capsules containing the 2 monomers which were irradiated at 0 h it was 42.26% for the capsules without the dye and 41.7 for capsules containing the dye. and in those irradiated at 24h it was 42.63% for capsules without the dye and 43.6 for those containing the dye.

For the capsules dissolved in water the amount of residue present for the dissolved alginate capsule was 45.85%, that for the dissolved alginate-PEGDMA irradiated at 0h was 40.223%, and that for the capsules irradiated at 24h was 44.44%.

So, in the capsules containing the two types of monomers the amount of calcium was similar. However, due to the variation in the dissolution % it is proposed that the form of incorporation of calcium in each case is different. Since the ones irradiated at 0h were more soluble it is proposed that the calcium here is not really incorporated in crosslinking and can't really form crosslinks between alginate chains since

the PEGDMA is directly polymerized and crosslinks trapping calcium inside the structure. On the other hand, when the capsules are irradiated after 24h the calcium has enough time to form crosslinks between the alginate chains before the photopolymerization of the PEGDMA takes place and that is why these capsules are less soluble.

The capsules containing the dye when compared to the capsules without the dye it was shown that the differences were negligible, so the presence of the dye didn't really affect the amount of the calcium in the capsules or the reaction between the calcium and the alginate chains.

7. BOD

After the 5-day incubation period finished, the values of the BOD can be read. It was shown that the solution containing the dissolved alginate capsules had the lowest BOD value of 13mg/l while the solution containing the dissolved alginate-PEGDMA capsules irradiated at 0h had the highest value of 27 mg/l and those irradiated at 24 h had a value of 21 mg/l.

According to the environmental protection agency (EPA) guidelines for water reuse, it was specified in most of the cases that for wastewater to be reused in urban, industrial or environmental sectors the BOD must be less than 30mg/l[29]. in this case we can observe that the different types of capsules do not go above this limit; so, adding another type of monomer in this case is not affecting the water quality.

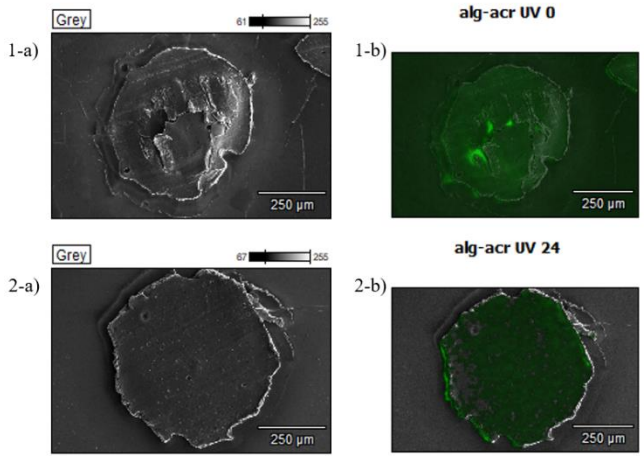

Figure 5: a) FESEM photos b) Map showing the distribution of calcium ions for 1) alginate-PEGDMA-dye capsules irradiated at 0h and 2) alginate-PEGDMA-dye irradiated at 24h

8. FESEM

The results obtained from this test show that the distribution of the calcium in each of the capsules is different. In the first sample which was irradiated directly and that contained a hole in the middle according to the ESEM pictures, the calcium was found to be mainly distributed inside the capsules on the boundaries of the hole (Figure5.1-b). On the other hand, the capsules irradiated after 24 h and which had a more homogeneous structure had the calcium distributed on the boundary of the capsule (Figure 5.1-b).

Conclusion

Three types of capsules were prepared to encapsulate a dye having different shell material: the first one was made only of sodium alginate and crosslinked through calcium ions, the second one was made of sodium alginate and PEGDMA which was polymerized under UV light and in the presence of an initiator directly after the capsule shape formation in the calcium chloride solution, and the third type consisted also of sodium alginate and PEGDMA where the capsules were left for 24 hours in the calcium chloride solution after which it was irradiated using UV light. The capsules irradiated directly showed an empty core and a heterogeneous structure while those irradiated after 24h showed a more homogeneous structure. Also, there was a difference in the mechanical properties where alginate capsules appeared to be stiffer and there were different rupture mechanisms. All these different properties which can be attained without compromising the biodegradability character open a door on these types of capsules to be used in different applications.

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