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Development of a Microfluidic Device to Encapsulate Isocyanate for Autoreactive and Ecological Adhesives

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Abstract. Present study was performed to explore a microfluidic approach for production of microcapsules (MCs) with polyurethane/polyurea shells containing isophorone diisocyanate (IPDI) in the core, for adhesive formulations. The MCs were produced, in a continuous mode, by a system involving a microfluidic device, containing a T-junction where is originated a monodisperse oil-in-water emulsion, followed by interfacial polymerization at the emulsion droplets surface. The resulting MCs are intended to be added to an adhesive base, leading to an autoreactive and ecological monocomponent adhesive, with high potential application. The MCs' morphology and size distribution were evaluated by scanning electron microscopy (SEM) and the results obtained by Fourier transformed infrared spectroscopy (FTIR) revealed a successful encapsulation of IPDI. The advances achieved in the current study will be a potential contribution to the innovation and development of new production methods and eco-friendly products.

1. Introduction

One of the current challenges in science is the development of safer new materials/processes for both human health and the environment, in order to promote sustainability and the improvement of the living conditions of future generations [1,2].

Microencapsulation is a process by which individual particles or droplets of an active agent can be stored within a shell, surrounded or coated with a continuous film of polymeric material. This is a growing field that has found application in many areas such as food, medicine, pesticides, environmental and biological engineering, cosmetics and coatings [3]. Moreover, microcapsules (MCs) were also used in adhesive, which could control release of additives and adhesives at the right time and the right place and improve the compatibility of certain ingredients to broaden their application fields [4].

Encapsulation of specific chemicals can be used to protect active agents from detrimental conditions (heat, light, humidity and exposure to other substances over their lifetime), shield an irritating smell, act as a carrier system, control the rate and moment at which the encapsulated compound is released, prevent the evaporation of volatile compounds and reduce the toxicity of



certain active substances [5]. Nowadays, the most reactive encapsulations are performed in batch processes to produce MCs. However, in this kind of processes, because of the highly variable shear used, the sizes and morphologies of the resultant microcapsules can vary enormously [6].

Microfluidics offers an alternate and versatile route to overcoming the limitations of batch processes. In microfluidic devices, the drops are produced in series, contrary to bulk emulsification methods where drops are formed in parallel under the influence of an external shear, which led to a greater control over size and polydispersity of the emulsified drops compared to bulk emulsification methods [7]. In addition, this technology offers other advantages such as reducing the consumption of reagents/samples to pico-liters; decreasing the reaction time to seconds; reducing waste generation; allowing rapid diffusion, mass and heat transfer [7, 8, 9].

Since isocyanates have a good performance in terms of bonding property, water resistance, aging-resistant performance and fine manufacturability, it has been widely used in the field of coatings and adhesive [10]. There are, however, several safety issues as well as potential risks to the environment and human health associated with the use of isocyanate adhesives, in particular when it comes to the direct contact of workers with isocyanate. Therefore, there is an urge to develop a green approach that still allows the use of isocyanate, but without exposure to it.

The goal of this study was the development of a microfluidic device to synthesise MCs with polyurethane/polyurea shell containing isophorone diisocyanate (IPDI) in the core as a self-curing agent. The IPDI was encapsulated through interfacial polymerization between a mixture of IPDI and a methylene diphenyl diisocyanate (MDI) pre-polymer, via stabilized oil-in-water (O/W) emulsion with gum Arabic as a prediluted emulsifier in the aqueous phase, in a microfluidic device. The resulting MCs are intended to be added to an adhesive base.

The proposed method has advantages of being readily controlled, cost-effective and easy to operate, together with its ability to produce a narrow MCs size distribution. By microencapsulating the reactive agent, the product is safer for handling by the industry operators, and the activation mechanism can be controlled more precisely

2. Materials and methods

2.1. Reagents

The chemicals used in this study include methylene diphenyl diisocyanate, MDI, isophorone diisocyanate, IPDI, gum Arabic, lime and glycerol. MDI prepolymer was obtained from CIPADE, IPDI was obtained from Acros Organics, lime was obtained by Lacrilar, gum Arabic and glycerol were obtained from Fisher Chemical. All chemicals were used in the experiments without further purification unless otherwise specified.

Arabic Gum was intended not only to stabilize the emulsion by its action as surfactant, but also to react with the isocyanate as a precursor to the wall of the MCs. The aqueous phase was prepared in a 250 mL beaker, at room temperature, and the solution was stirred in a magnetic stirrer plate during 1h. MDI prepolymer was vigorously mixed with IPDI to yield the oil phase. In some experiments (2nd formulation) glycerol and lime were used to decrease the quantity of gas produced in the reaction, being added to the aqueous solution.

2.2. Microfluidic Device

In the microencapsulation process there are 5 main steps (Figure 1): the first one consists in the preparation of the phases (aqueous and organic) and then a peristaltic pump will pull the reagents that are inside of microtubes, up to the T-junction, where the emulsion is formed. After this, MCs will be formed during their passage in a plastic coil that is inside a thermal bath. Then, the last step, filtration, occurs.

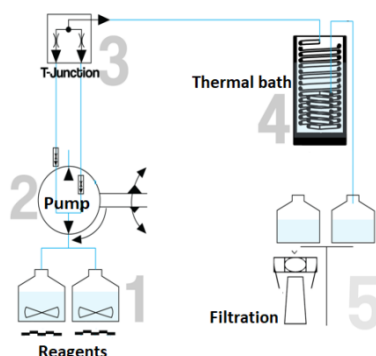


Figure 1. Steps of the microencapsulation system.

The microencapsulation system developed in this work is composed of the following components: (1) heating plates that maintain the reagents homogeneous and at the required temperature; (2) a peristaltic pump which has advantages such as no contamination, low maintenance needs, ability to handle a large variety of fluids, versatility and ease of cleaning ; (3) a T-junction (Figure 2), produced by 3D printing, using a EDEN 260V 3D printer with 600 dpi precision and 0.016 mm layer thickness, with a photocurable polymer as the building material and a water-soluble support material; (4) a thermal bath, set at 60 °C, including an immersed serpentine tube, wherein the MCs flow; (5) a filtration system, composed by a kitasato, a funnel and a vacuum pump.

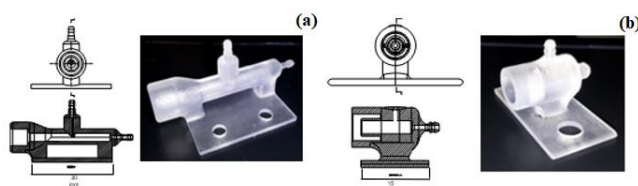


Figure 2. Initial (a) and final (b) concept of T-junction.

In Figure 2 it's possible to see the evolution of T-junction structure. The improvements in relation to the initial concept go through the last one occupied less space, presents better connections with the respective tubes and allows the production of smaller MC's. In T-junction the aqueous phase comes horizontally while the organic phase comes from above, and this is the point where the emulsion's formation starts.

2.3. Characterization

The characterization of the obtained MCs was performed using different techniques such as optical microscopy, scanning electron microscopy (SEM) and Fourier transformed infrared spectroscopy (FTIR).

Morphology observation. SEM analysis was carried out to evaluate the morphology and roughness of the obtained MCs. SEM images were collected in a JEOL JSM7001F (JEOL, Tokyo, Japan) microscope with a FEG-SEM (Field Emission Gun) system. Before the analysis, the MCs were placed in a sample holder using conductive adhesive tape with double face. Afterwards, a conductive Au/Pd thin film was used to coat the samples, through sputtering, using a Quorum Technologies sputter coater model Q150T ES. The MCs obtained were also used to evaluate the MCs' size distribution using the software ImageJ.

FTIR spectroscopy analysis. FTIR analyses were used in order to verify the functional groups present in the obtained MCs. The spectrum was analyzed, and the main peaks were identified (absorbance as a function of wave number). This analysis was performed in a PerkinElmer, Spectrum Two, FTIR spectrometer, equipped with a Pike Technologies MIRacle® 189 Attenuated Total Reflectance (ATR) accessory. The spectra were obtained with a resolution of 4 cm⁻¹ and data collection of 8 scans, over a frequency range of 400-4000 cm⁻¹.

3. Results and Discussion

O/W isocyanate containing MCs were produced in a microfluidic device using IPDI/MDI prepolymer in the O phase and water/gum Arabic in the W phase.

In the first experiments performed (1st formulation), the presence of gas bubbles both in the serpentine and inside the MCs was noticed, leading to the MCs agglomeration inside the serpentine and even to the MCs bursting due to the expansion of the gas present in its interior. After a careful observation of the MCs inside the serpentine, it is believed that small bubbles of gas were already formed inside the MCs at the T-Junction, probably due to the residual air dissolved in the W phase or the reaction of the isocyanate with the W phase, forming urea and the release of CO₂ (g). This phenomenon was not observed in the batch process, since the shear stress due to the high-speed agitation releases CO₂ (g) into the atmosphere. In the microfluidic system, the reaction occurs in a confined way, within the serpentine, preventing the CO₂ escape. In order to minimize the formation of gas bubbles during the MCs synthesis, the W phase composition was optimized, by adding lime and glycerol (2nd formulation). The use of lime (CaO) has two purposes: (1) remove CO₂ bubbles (g) and (2) produce fine calcite that may diffuse as a charge on the MCs PU walls and increase its impermeability, through "filtering control" mechanisms [11].

3.1 Effect of the addition of glycerol and lime in the aqueous (W) phase

Figure 3 shows a comparison of the obtained MCs before and after the problem of gas bubbles was solved. As it is possible to confirm, without the gas formation it was possible to obtain smaller and spherical MCs, with a narrow size distribution.



Figure 3. MCs obtained in 1st (left) and 2nd formulation (right).

3.2 Characterization of the obtained MCs

A morphological analysis of the MCs was accessed through SEM, whose photomicrographs are shown in Figure 4. The MCs are found to exhibit a spherical shape, however with some irregularities. Some of the MCs were tried to be crushed, in order to access the MCs morphology, however it was not possible, probably due to the high stiffness and/or thickness of the MCs wall (shell).

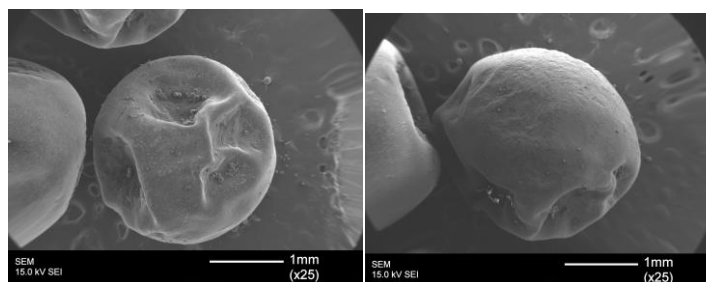


Figure 4. SEM images of MCs.

Through ImageJ software, it was made an analysis of the size distribution of the MCs obtained by 2nd formulation, concluding that the particles have an average diameter of $1100 \pm 90 \mu\text{m}$. The size of the

MCs is herein found to be bigger than desirable, so it is necessary to adjust the O and W flows in order to obtain smaller MCs. Quevedo et al. [12] studied the effect of aqueous flow rate on capsule size by holding the organic disperse flow rate constant and by varying the aqueous flow rate. They concluded that capsule size gradually decreased with increased aqueous flow rate and, hence, with increasing Reynolds number. So, the next step is performing the experiments with a higher W flow rate.

Samples of MCs obtained by microfluidic device were characterized by FTIR spectroscopy analysis and compared with the spectrum obtained from similar MCs synthesized by conventional emulsion/interfacial polymerization (batch process), under the same conditions, in another lab, by other members of the team. Figure 5 shows the respective spectra. In general, all the spectral features characteristic of polyurethane, polyurea and isocyanate materials are present in the three analysed samples.

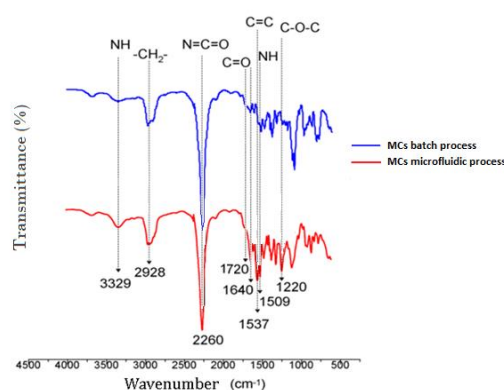


Figure 5. Comparison of FTIR spectra of MCs obtained in batch and microfluidic processes, with identification of the main peaks.

From the FTIR spectra, shown in Figure 5, it is possible to observe an intense band peaked at ca. 2260 cm^{-1} , related to the $\text{N}=\text{C}=\text{O}$ bond stretching vibration, which indicates the presence of unreacted NCO groups in the MCs, confirming a successful encapsulation of IPDI. The peaks ascribed to the presence of amine groups can be observed at 3329 cm^{-1} from N-H stretching of the amine bonds and at 1509 cm^{-1} from N-H bending. Concerning the bands at 2928 and 1537 cm^{-1} , the first one is attributed to the asymmetric stretching vibration of the $-\text{CH}_2$ group (aliphatic bonds of MDI or IPDI) while the second is attributed to the symmetrical elongation vibration of the $-\text{CH}$ (phenyl groups of MDI). The bands at 1640 and 1210 cm^{-1} correspond to a $\text{C}=\text{O}$ group from urea and a $\text{C}-\text{O}-\text{C}$ group from urethane. The band at ca. 1720 cm^{-1} corresponds to the $\text{C}=\text{O}$ group from urethane moieties. The exhibited FTIR spectra reveal the formation of a polyurethane/polyurea MC's shell and an effective isocyanate (IPDI) encapsulation.

A relative measure of the isocyanate's encapsulation efficiency was calculated, considering the peak at ca. 2260 cm^{-1} assigned to NCO stretching (wavenumbers in the range of 1926 to 2444 cm^{-1}) and the area of the peak at 1300 cm^{-1} assigned to C-O stretching, typically related to the PUa / PU shell material, which does not tend to suffer significant changes over time. The equation 1 was applied to obtain the relative encapsulation yield, considering the referred areas, previously calculated through the OriginPro 9 software.

$$Y = \frac{\text{Area}_{2260\text{ cm}^{-1}}}{\text{Area}_{1300\text{ cm}^{-1}}} \quad (1)$$

Where Y is a relative encapsulation yield, which represents an indirect measure of the encapsulation efficiency. The $\text{Area}_{2260\text{ cm}^{-1}}$ and $\text{Area}_{1300\text{ cm}^{-1}}$ correspond to the areas of the peak related to the NCO group and to the C-O stretch, respectively. The Y values of the MCs obtained by

the batch process and by microfluidic process are 47,6 and 19,6, respectively. The MCs synthesized by batch process have shown more encapsulated IPDI.

4. Conclusions and ongoing work

This research provides a new method for synthesizing monodisperse isocyanate MCs. The microfluidic device allows the fabrication of the microcapsules one at a time and offer robust and precise control over the external dimensions.

Since the obtained MCs are bigger than desirable, it is necessary to perform the experiments with a high W flow rate, in order to obtain MCs with a small diameter. Through the characterization by FTIR it was possible to conclude the efficiency of IPDI's encapsulation.

The generated MCs have a potential use in different areas, namely aeronautic and automobile industries, where they are expected to release the isocyanate under specific and controlled conditions, such as pressure or/and temperature. Thus, the use of a microfluidic device for producing isocyanate MCs, may be considered as an important path for both academic and industrial applications.

The incorporation of obtained MCs in adhesives will be studied. Further studies are still in need, regarding the MCs properties and the test of different configurations for the T-junction, in order to reach optimized MCs.

Acknowledgments

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