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Research Article

Factors affecting the synthesis of microcapsules containing polyisocyanate with interfacial polymerization in water-in-oil microemulsion

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ABSTRACT

Multi-Microcapsules containing polyisocyanates such as TDI and IPDI have been considered for a variety of applications such as self-healing materials and coatings, prepare foams, composites, single-component adhesives, and most recently curing of polyurethane binder system. Interfacial polymerization in water-in-oil microemulsion is a quick and Inexpensive method for microencapsulation of polyisocyanates. In this paper, the effect of factors affecting the synthesis and properties of polyisocyanate microcapsules, include solubility of active hydrogen source in the oil phase to the water phase, type of monomer used, surfactant, solvent, synthesis temperature, stirring speed and emulsification time, on thickness, hardness, permeability and growth rate of the shell, as well as diameter, core fraction and particle size dispersion of microcapsules and reaction time have been investigated. The use of microcapsules containing polyisocyanate in various applications requires the satisfying of functional requirements. By controlling the factors affecting the process, microcapsules with the desired properties can be prepared.

Keywords: Microencapsulation; Isocyanate; Self-Healing; Interfacial Polymerization; Pot-Life.

1. Introduction

Encapsulation is defined as the technology of enclosing solids, liquids, and gases in small enclosed capsules. The purpose of microencapsulation of reactive materials is to achieve the ability of controlling the reaction. In summary, microencapsulation is done for three purposes: 1- Protection of core material from unfavorable environmental effects (pH, temperature, humidity, etc.) 2- Control of active compounds for delayed or long-term (stable) release 3- Combining two incompatible compounds to obtain a multifunctional structure [1]. The most remarkable feature of microcapsules is their microscopic size, which gives a huge surface area that can be accessed by 94 absorption or repulsion, chemical reactions, light scattering, etc. Another significant advantage of microcapsules is the ability to hold the core material and protect it from the environment and releasing the core material in the proper position if needed. [3]. Due to the diverse products and wide applications that polyisocyanates have in scientific research and various industries, like adhesives, rubber and composites, microencapsulation of polyisocyanates enables the development of new types of materials and systems with special capabilities [4]. So far, microencapsulation of polyisocyanates has been used in the applications of self-healing materials, anti-corrosion coatings, one-component polyurethane adhesives, and more recently for the curing of binder system [4-7].

2. Experimental

2.1. Interfacial polymerization in water-in-oil microemulsion

The interfacial polymerization method in water-in-oil emulsion has been introduced as a suitable method for microencapsulation of polyisocyanates such as toluene diisocyanate (TDI) and Isophorone diisocyanate (IPDI) in various references [4, 8, 9]. Interfacial polymerization developed in the late 1960s and its application to microencapsulation technology dates back to

the mid-1970s. The main feature of this process is the interfacial diffusion of reagents, in which a solution of a multifunctional monomer as the core material is dispersed in an aqueous phase. By adding a reagent to the dispersed monomer in the aqueous phase, polymerization begins at the droplet surface. Encapsulation is done by forming a shell around the dispersed droplets [1, 2]. The process of microencapsulation of polyisocyanates using Interfacial polymerization in water-in-oil microemulsion consists of three main steps: 1- Preparation of emulsion 2- Adding active hydrogen source-Completing the shell 3- Separating, washing and drying the microcapsules; which is described in detail in various references [8, 10].

3. Results and discussion

3.1. Solubility of active hydrogen source

Polyols and amines are both normally soluble in the aqueous phase and strongly affect the thickness and morphology of the shell. The solubility of amines and polyols in the organic phase and the aqueous phase can be defined as their separation constant (Equation 1). In this equation, [amine] O and [amine] W are the equilibrium concentrations of amines in the oil and water phases, respectively. This equation also applies to the polyols. As the KOW increases, the shell thickness also increases (Figure 1). This phenomenon can be explained by the higher diffusion rate of amine or polyol molecules towards the organic phase than the aqueous phase during shell formation [9, 11, 12]. This factor can also affect the minimum reaction time [13].

Equation 1: KOW=[amine] O/[amine] W

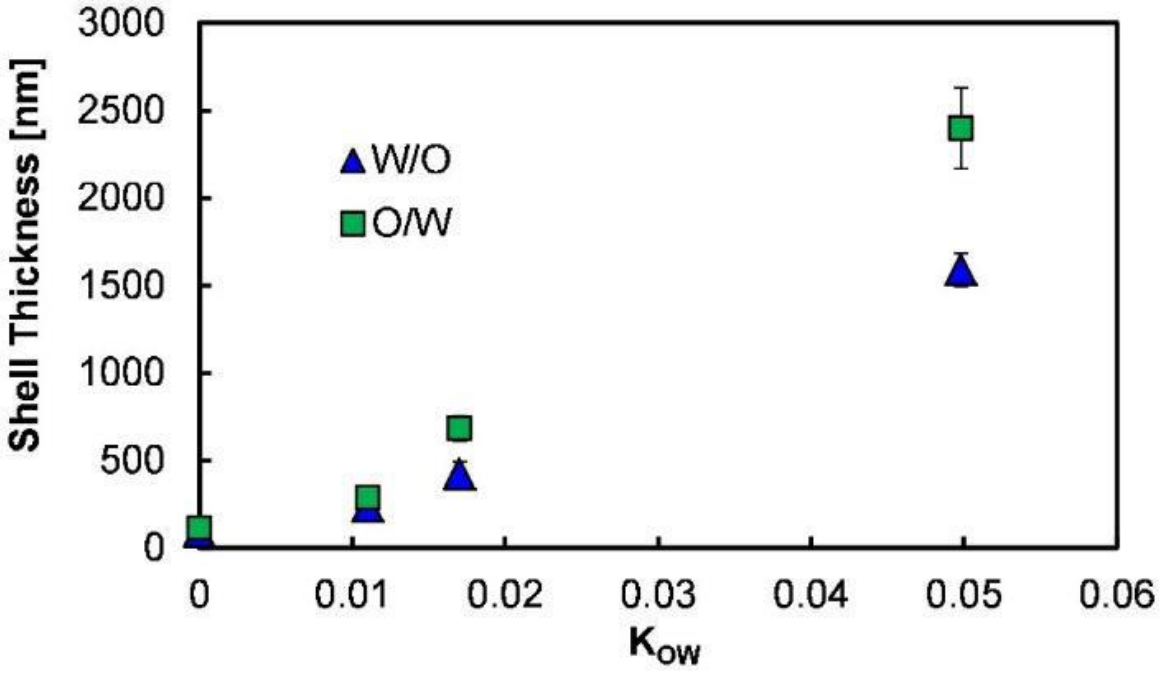

Fig.1: The thickness of the shell increases with increasing solubility of active hydrogen source [12].

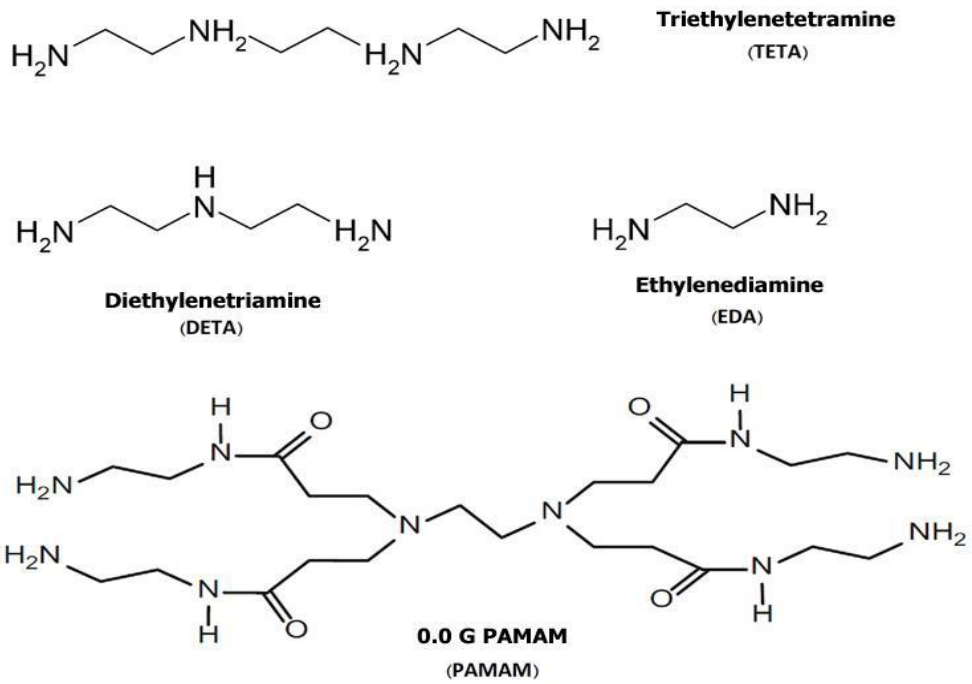

Fig. 2: Molecular structure of several different polyamines [16].

3.2. Chemical structure of active hydrogen source

The chemical structure of polyamine and polyol can dramatically determine the morphology of microcapsules. In general, compounds with more OH or NH groups, form a crosslinked network, resulting in a more rigid shell. Linear structure active hydrogen sources result in lower shell strength with Wrinkled appearance. Active hydrogen source with spatial inhibition of molecular structure, when compared to reactants with less active hydrogen groups, result in thicker shell. For example, microcapsules formed in the presence of DETA and TETA have a wrinkled, relatively thin shell, while the addition of 0.0 G (PAMAM) results in better microcapsule shell morphology. This may be due to the higher NH factor in PAMAM, which results in more crosslinking (Figure 2) [9, 14, 15]. EDA has been reported to diffusion faster than DETA due to its short molecular chain. This somehow destroys the emulsion stability, creates a thick, rough shell, and creates microcapsules of non-uniform sizes. But there is a slower release for DETA, which is also due to its longer molecular chain length. When DETA reacts with a polyisocyanate, it produces branched polymer and increases emulsion stability. The number of hydrophilic moieties in the amine plays an important role in the microcapsule microstructure [17]. The average diameter and particle size dispersion of the microcapsules are also affected by the chemical structure and properties of the active hydrogen sources, so more NH or OH groups and higher molecular weight results in larger microcapsules and larger average particle size (Figure 3). [15].

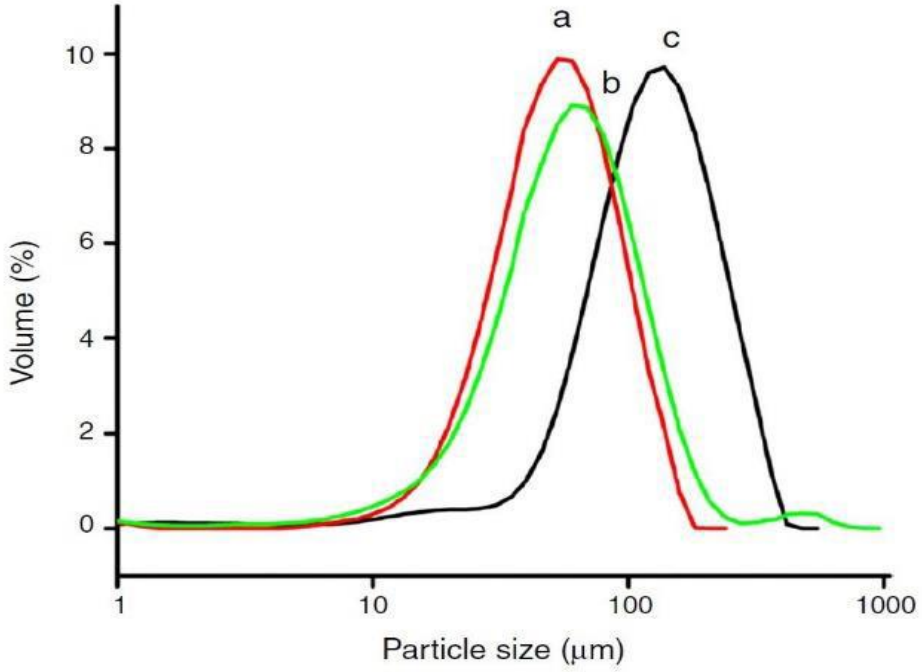

Fig. 3: Particle size obtained by different types of amines: a) DETA, b) TETA, c) PAMAM [15].

3.3. Concentration of active hydrogen source

The thickness of the shell increases with increasing concentration of amine or polyol, and to a lesser extent with increasing concentration of polyisocyanate (Figure 4). This finding indicates that a threshold amount of polyisocyanate is required for complete shell formation [11].

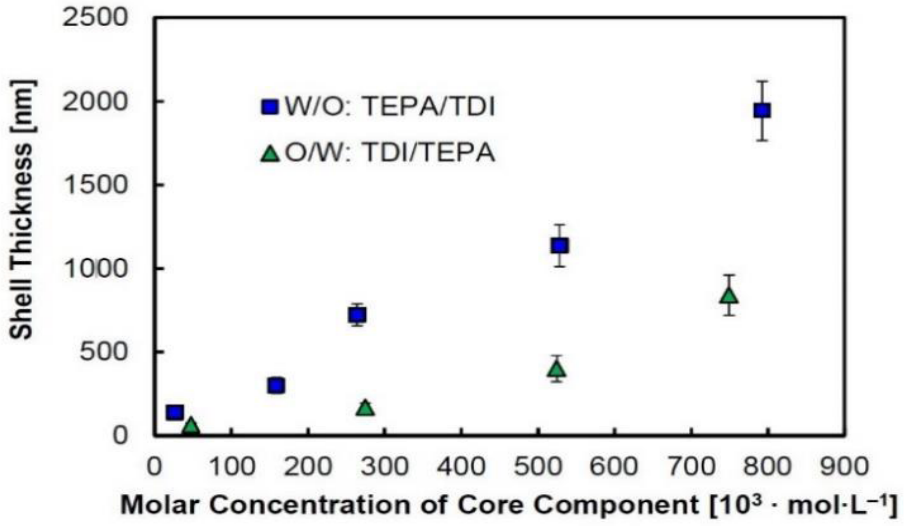

Fig. 4: Shell thickness versus Molar concentration of core component [12].

3.4. Surfactant

Increasing the amount of surfactant can increase the growth rate of the microcapsule shell by increasing the dissociation constant and transferring active hydrogen source to the organic phase. The presence of the right amount of surfactant stabilizes the emulsion and prevents the microcapsules from accumulating during the process. Higher concentrations of surfactant reduce droplet size, reduce particle size dispersion, and in some cases increase emulsion stability. As the amount of surfactant increases, the surface tension decreases and the diameter of the final microcapsules decreases. However, when the critical micelle concentration (cmc) is reached, the diameter of the final microcapsules reaches a constant limit. This value for Arabic gum surfactant is about 3% by weight (Figure 5) [1, 6, 18].

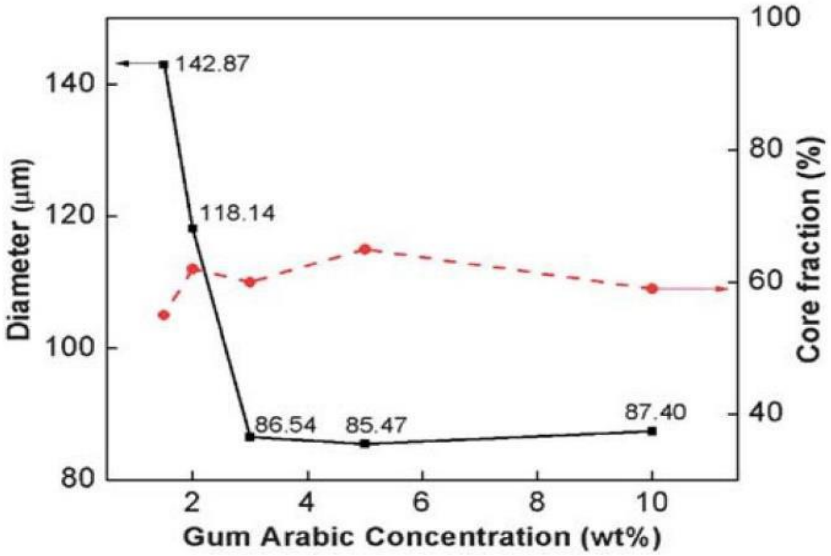

Fig. 5: Effect of surfactant concentration on particle diameter and core fraction [6].

3.5. Organic phase structure

Aromatic or aliphatic structure, as well as the linear or branched structure of polyisocyanate, can affect the porosity and permeability of the microcapsule shell and, consequently, the microcapsule release performance. In addition, multifunctional reactants can improve the thermal and mechanical stability of microcapsules by forming a three-dimensional lattice polymer. For polyurea and polyurethane microcapsules, the use of multifunctional isocyanates is preferable because it results in the formation of less permeable microcapsules. This phenomenon is due to the limitation of hydrolysis of polymeric isocyanate groups, which reduces CO2 emissions and thus reduces the porosity of the polymer shell [1, 9]. Microcapsules prepared from TDI-glycerol prepolymer had been reported that showed superior chemical, morphological, and thermo-gravimetrical properties. When these microcapsules incorporated into a coating in the concentration of 20% wt., provided longer and more efficient anticorrosion protection [19].

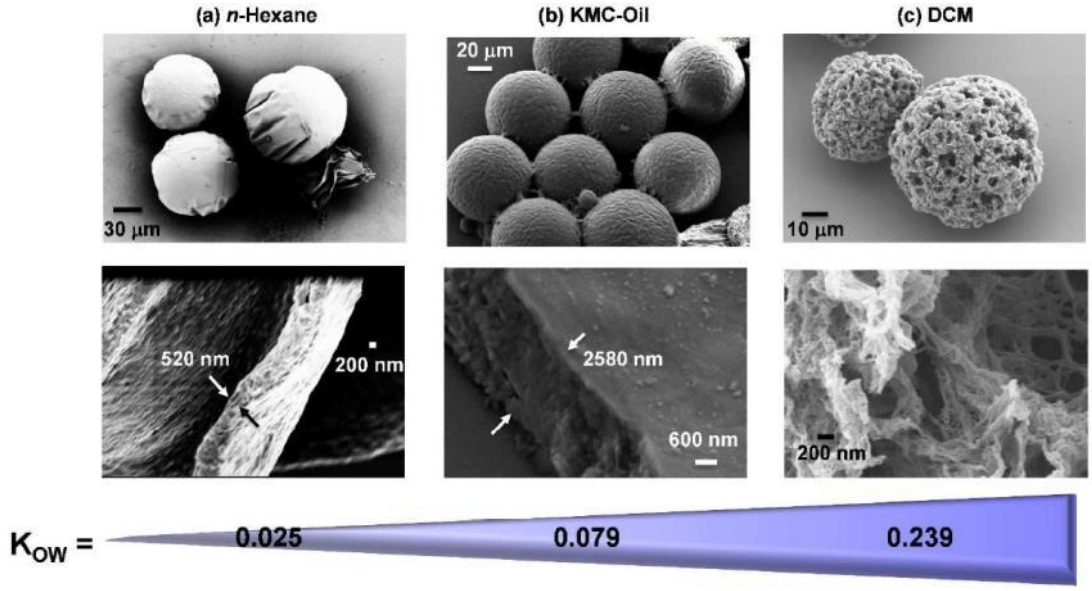

Fig. 6: Effect of solvent on diameter and morphology of microcapsules [11].

3.6. Solvent

The solvent can affect the formation of microcapsules by changing the surface tension of the medium. Therefore, it can affect the diameter and morphology of the surface of the obtained microcapsules. Especially when the amount of solvent increases, the diameter of the microcapsules decreases sharply. This phenomenon is due to the reduction of viscosity of polyisocyanate compounds by the addition of solvent. Thus, the higher the solvent concentration, the smaller the oil droplets in the emulsion, resulting in smaller microcapsules. The solvent also affects the contact area between the polyisocyanate and the active hydrogen source, leading to heterogeneous reaction kinetics. Evaporation of solvent during the drying stage also affects the morphology of the microcapsules [13]. In addition, an organic solvent can change the rate of reactions by changing the diffusion of monomers into the complementary phase. Some organic solvents such as toluene and chloroform can be used to improve the diffusion, while n-hexane can reduce the diffusion [1, 11].

3.7. Ccore/Cshell ratio

This ratio determines the amount of material to be encapsulated and the amount of material that is added to form the shell. This ratio also determines the size of the microcapsule, the morphology and thickness of the shell, and the efficiency of the microencapsulation process. Some references indicate that the best Ccore/Cshell ratio in terms of higher microencapsulation efficiency is 77/23 [20]. It has also been reported that as the Ccore/Cshell ratio decreases, the size of the microcapsules increases. An external diffusion mechanism has been proposed to explain this phenomenon. According to this mechanism, polyisocyanate migrate through the formed shell and some of them react with water and form amines, then react with additional polyisocyanates and cause the accumulation of polyurea on the surface of the shell. As this process continues, the shell becomes thicker and the size of the microcapsules becomes larger [1].

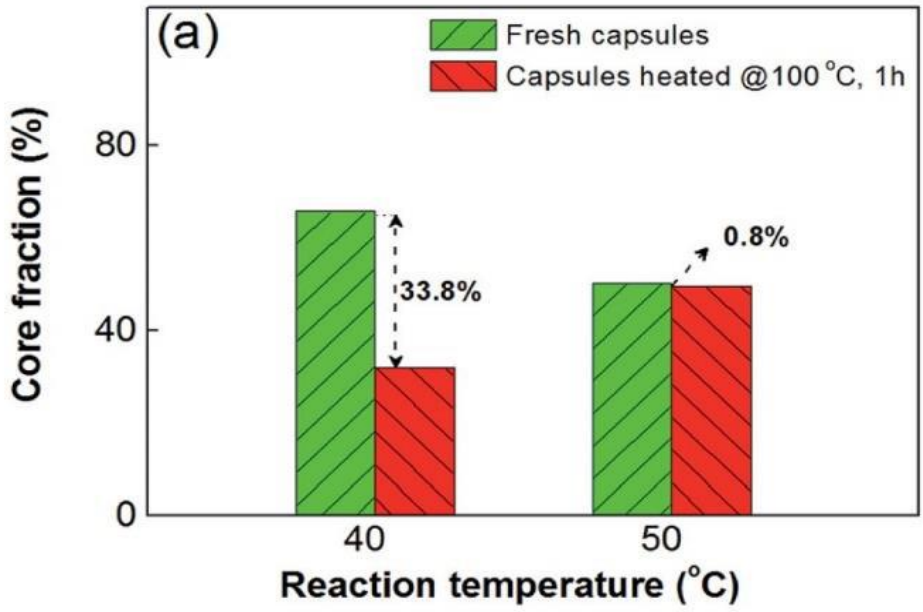

Fig. 7: Effect of reaction temperature on the core fraction of microcapsules [21].

3.8. Synthesis temperature

Increasing the synthesis temperature increases the formation of the polymer shell by increasing the diffusion rate of the monomers and increasing the reactivity of the material. Higher reaction temperatures also lead to the formation of denser shells, with lower permeability, and more thermally stable microcapsules, but reduce the mass fraction of the core [1, 21].

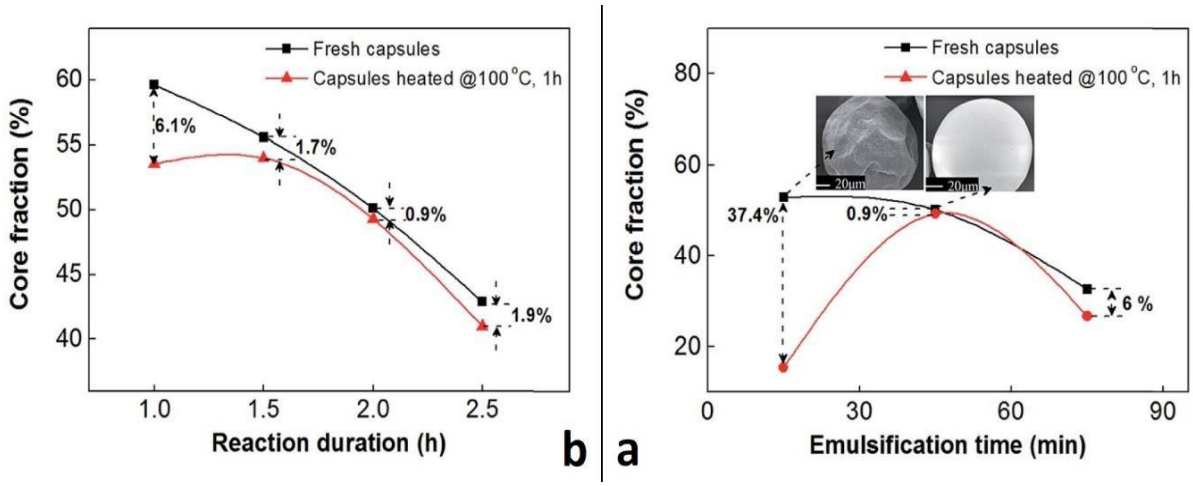

Fig. 8: The effect of a) emulsification time and b) reaction duration, on the core fraction [21].

3.9. Emulsification rate and duration

In one case, it was observed that by increasing the emulsification time from 15 to 75 minutes, the core fraction of fresh microcapsules decreased from 52.8% to 32.6%. The cause of this phenomenon is the consumption of more core material by water for a longer period of time. Also, the core fraction of the obtained microcapsules was reduced by 37.4% (from 52.8% to 15.4%) after 15 minutes of isothermal conditions at 100 ℃ after 60 minutes of emulsification. Subsequently, the release of the core material after the isothermal process was gradually reduced to a minimum of 0.9 for microcapsules prepared within 45 minutes of emulsification. After this limit, the release of the core material after the isothermal process

gradually increased, increasing the emulsification time from 45 to 75 minutes. This means that increasing the emulsification time results in a smoother and denser shell, but by passing an optimal value, due to the hydrolysis of the outer layer, the release of the core material increased during the isothermal process. However, as the emulsification time increases, more CO_2 can be released, creating more cavities and creating an undesirable shell structure that can increase core release (HDI). The emulsification time and the optimal reaction period have been investigated by the authorities [21]. The properties of an emulsion largely depend on the emulsifier used. HLB1 and the chemical structure of a given emulsifier are important for emulsion stability. But not all emulsifiers have the same efficiency. Therefore, different emulsification rates can be achieved by changing the emulsifier. Higher emulsification rates reduce the size of microcapsules faster, but increase the particle size dispersion [1, 22].

Table 1: Diameter, shell thickness and ratio of shell thickness to diameter of microcapsules at different stirring speeds [8].

agitation rate (rpm)	500	700	900	1100	1500
D, diameter (μm)[a]	413 ± 124	205 ± 73	103 ± 34	67 ± 17	39 ± 9
h, wall thickness (μm)[a]	17 ± 4	10 ± 2	4 ± 2	3 ± 1	2 ± 0.5
h/*D*	0.04	0.05	0.04	0.05	0.05

[a] Average value ±1 standard deviation.

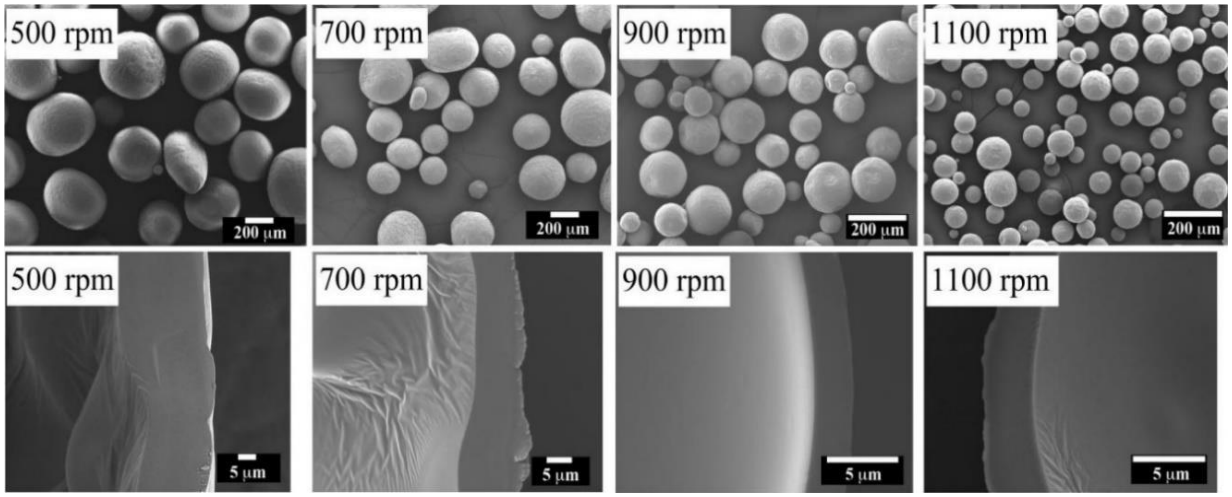

Fig. 9: The effect of stirring speed on diameter and shell thickness of microcapsules [8].

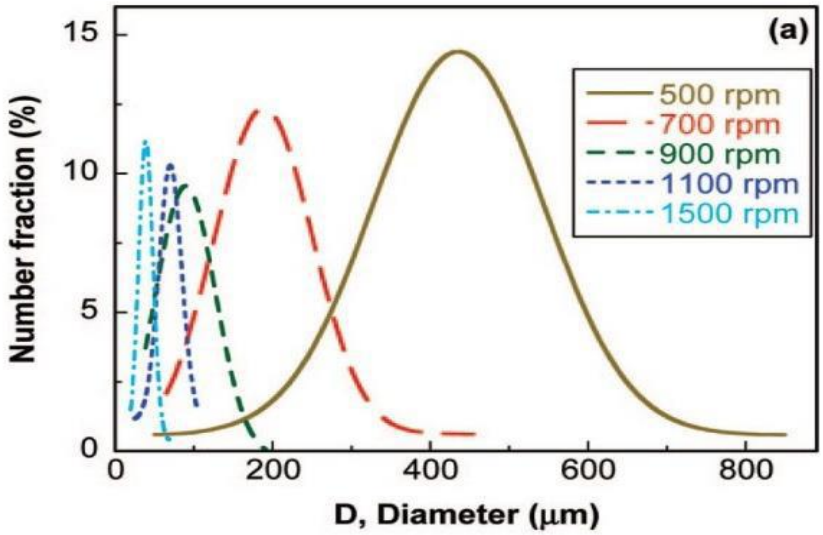

Fig. 10: Size dispersion of the microcapsules prepared at different stirring speeds [8].

3.10. Stirring speed

The reaction speed and reaction time increase by reducing the droplet size of the emulsion. Therefore, the higher stirring speed, in addition to dispersing the finer particle size, reduces the core content in the final microcapsule by reducing the droplet size. Very small microcapsules have a higher energy level and are thermodynamically unstable. Therefore, they have a great tendency to accumulate. Using the right amount of emulsifier with a proportional stirring speed

helps to reduce the accumulation of microcapsules. It is stated that when low stirring temperature and speed are applied to UF1 microcapsules, the encapsulation efficiency decreases due to the lack of proper dispersion of the oil phase, and the predominance of the reaction mainly in the aqueous phase relative to the oil/water interface [1]. Several studies have investigated the effect of stirring speed on microcapsule diameter, shell thickness and encapsulation efficiency [8, 23].

4. Conclusion

The use of microcapsules containing polyisocyanate in various applications requires the satisfying of functional requirements. For this purpose, the first step is to select the appropriate process, but the main challenge is to identify the parameters that affect the process, and then the optimal values or limits of these parameters for the intended application must be specified. Therefore, it is necessary to get an accurate overview of the subject before entering the experimental work. The suitable method for microencapsulation of polyisocyanates is interfacial polymerization in water-in-oil microemulsion. Factors affecting the synthesis process and properties of microcapsules containing polyisocyanate, include factors related to raw materials, their chemistry and concentration, and synthetic factors such as temperature, mechanical stirrer speed, emulsification rate and duration. Microcapsules with desired properties will obtained by designing and controlling the factors affecting the synthesis process.

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