Study of submicrocapsules structure stabilized by modified silica dioxide nanoparticles

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Abstract. In this research the structures of Miglyol 812 submicrocapsules, stabilized by silica dioxide nanoparticles, modified by oleic acid, were studied. It was found that the size distribution of silica particles modified with oleic acid depends on the amount of oleic acid. There is a limit to the ratio of oleic acid to silica at modification of silica particles with oleic acid. Experimental results have shown that the optimal ratio of oleic acid to silica is in the range from 1·10⁻² to 5·10⁻¹. The use of silica particles modified with oleic acid allows to obtain an emulsion with a 30 % of oil phase, with an average size from 80-300 nm. Thus, modification of hydrophilic silica particles with surfactants such as oleic acid in order to make them more hydrophilic and able to be adsorbed at the oil / water interface can be used to prepare a stable Pickering emulsion. As a result the stable Pickering emulsions which can be used for encapsulation of various substances were obtained, and the use of microcapsules allows one to decrease their impact on environment and increase efficiency of usage.

1. Introduction

Microencapsulation and controlled release of various active substances, for example agricultural chemicals, can help to reduce encapsulated agent toxicity, to reduce the impact of substances on the environment, and to improve agent efficiency and efficacy [1].

That is why microencapsulation has found a great application in agriculture as an active substances delivery system. The different plant protection products were microencapsulated, for instance, insecticides [2-4], herbicides [5-8], fungicides [9], essential oils pesticides [10, 11]. Also, microencapsulation of microbial cells [12] can help to prevent stress caused by environment and to increase their stability [13, 14]. Technologies of microencapsulation can improve the stability and residual action of bioactive substances, and this could increase their field use.

Thus, encapsulation is being attracting method because it improves cell’s stability and tolerance to inhibitors, increases the amount of biomass inside of reactor, and reduces the cost of cell restoration, utilization and further processing. There are many studies have reported on microencapsulation of active
ingredients by use of several methods including spray drying [15], simple coacervation [16], complex coacervation [17], emulsion extrusion [18] and supercritical fluid deposition [19]. However, these methods do not yet solve the problems of the duration of use due to unreliability of used capsules. Therefore further researches have to be carried out to find methods that allow to ensure mechanical strength of capsules and reliable release. For this, it is necessary to find methods that will ensure the mechanical strength of the capsules and reliable release.

This research aims to study the potential of emulsions, including Pickering emulsions, to maintain the effectiveness of various biocides in relation to pathogenic microflora for use in various industries.

2. Methods of research

In case of using oleic acid to modify the surface of silica nanoparticles the following procedure was used [20]. The Ludox TM-40 silica particles were ultrasonicated (Bandelin, Sonopuls HD 3100) for 10 min at 30 W power prior to use to avoid aggregation. The particle dispersion had a transparent and slightly bluish appearance. The oleic acid-water mixture was also ultrasonicated for 10 min at 30 W power to effectively disperse oleic acid in water as micrometer-sized droplets. Afterward, the proper amounts of this mixture were added to the silica particles suspension. The resulting sample was ultrasonicated at 30 W power in pulse mode (3 s pulses with 1 s pauses) for 10 min to provide further energy for mixing and adsorption.

To prepare the emulsions, the modified silica particle dispersions were transferred to a vial, to which water, and then the lipophilic phase, were added. For pure oil dispersions, 30% of the total volume was oil (Miglyol 812). The resulting mixture was ultrasonicated at 60 W to disperse the oil phase for 10 min, which led to a milky suspension. All measurements were performed at 25 °C.

3. Results and discussion

Figure 1 shows the mean diameter of silica nanoparticles by intensity. The results correspond with specification sheet of the product. Only one peak with maximum value at of 20-30 nm can be seen.

![Size Distribution by Intensity](image)

**Figure 1.** Size distribution by intensity of 5 wt. % dispersion of silica particles Ludox TM-40, nm.
These particles were modified by oleic acid. In Figure 2 the results of size distribution by intensity of 5 wt. % dispersion of silica particles modified by 12 mM oleic acid are shown. Measurements show that two more picks appeared.

According to DLS results the first pick corresponds to size of 36 nm, the second – 418 nm, and the third – 4.7 µm. The value of first pick can be explained by modification of separate silica nanoparticles by oleic acid, however the second pick might be aggregates of modified nanoparticles. There is the third pick with a 4.7 µm diameter that is most probably oleic acid droplets that were coagulated before modification of silica nanoparticles. It can also indicate that all silica particles were modified and there is a certain extra amount of oleic acid and it is possible to decrease amount of oleic acid.

The second pick can be emulsion droplets stabilized by silica nanoparticles that can be seen from SEM photograph (Figure 3).

However, the results of size distribution by volume show that in case of modified particles the number of particles with size of 418 nm and 4.7 µm can be neglected because of its extremely small amount (Figure 4).
Figure 4. Size distribution by volume of non-modified and modified silica particles, nm. Red - 5 wt. % dispersion of silica particles, green - 5 wt. % dispersion of silica particles modified by 12 mM oleic acid.

Considering red line (Ludox TM-40 nanoparticles) and the highest pick of green line (silica particles modified by 12 mM oleic acid) it can be seen that the diameter of separate silica nanoparticles increased from 22 to 36 nm that indicated success of the modification process. The experimental results showed the formation of uniform emulsion with white colour and average size of droplets of 350 nm. Comparing (Figure 5) modified silica particles size (green line) with emulsion droplets size (red line) by intensity it can be clearly seen that the number of particles with the diameter of 36 nm reduced significantly, meanwhile the pick corresponding to particles with the diameter of 300-400 nm increased.

Figure 5. Comparison of silica particles modified by 12mM oleic acid and emulsion obtained using these particles. Green – modified silica particles 5% with 12mM oleic acid; Red – Miglyol 30% submicrocapsules stabilized with 5 wt. % dispersion of silica particles modified by 12 mM oleic acid

4. Conclusion
Thus, emulsions were prepared using silica nanoparticles modified with oleic acid. Experimental results showed that use of modifier leads to formation of stable emulsions with a diameter of 80 – 300 nm. The presence of more than one picks says that it is necessary to adjust the optimal ratio, and modification and emulsification modes.

On the basis of experimental results Middle chain triglyceride Miglyol 812 allowed one to obtain stable Pickering emulsion that can be used for encapsulation of various substances, and use of microcapsules allows one to reduce their impact on environment and increase efficiency of using.
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