Preparation of Polymer Microcapsules by Using Biodegradable Aliphatic Copolyesters Based on Dimerized Fatty Acid

Agnieszka Kozlowska

Abstract— The article presents the results of research on the possibility of obtaining microcapsules by coacervation. The polymeric shells used were multiblock, biodegradable, aliphatic polyesters. These were copolymers based on succinic acid, sebacic acid and dimerized fatty acid. It was investigated how the mixing time affects the quality of the obtained microcapsules without the core, and then different types of capsule filling were used.

Index Terms— microencapsulation, coacervation, polyester, succinic acid, sebacic acid, dimerized fatty acid, poly(butylene succinate).

1 Introduction

Microencapsulation is currently one of many very dynamically developing technologies. It is increasingly finding practical applications in various industries, including in the food, cosmetic, textile, biomedical, pharmaceutical, petrochemical, agricultural and plastic products industries [1,2]. This technology enables, among others immobilization of very small, microscopic amounts of substances in the capsules, which constitute the so-called core. The coatings are formed of one or several different polymers, by means of specific chemical reactions and physical processes [3].

A suitable selection of polymers used as the coating material allows the release of the substance encapsulated in the microcapsule in a controlled manner. In order for this process to be possible as a shell material, polymers with different solubility and porosity as well as biodegradability are used [4,5].

Microencapsulation offers increased selectivity, the ability to co-immobilize several components simultaneously, and a controlled connection with the substrate. Separation of active substances from the external environment promotes the increase of resistance to external factors and often also changes the value of the optimal pH. Microscopic dimensions make it possible to build a huge work surface. In addition, this process protects substances that are immobilized prior to deactivation, degradation and flocculation. A number of microencapsulation methods have been developed. However, it should be remembered that each of them can be subjected to numerous modifications, which increases the diversity and scope of application [6].

An important advantage of polymeric microcapsules is the possibility of obtaining controlled degradation by operating the composition and structure of the polymer so that the degradation takes place in a specific place, e.g. the digestive system. They can therefore be applied to the controlled release of drug substances at a specific place and time (DDS - Drug Delivery System) [1-7].

The aim of the presented study was to investigate the influence of the variable proportion of butylene polyesters of dimerized fatty acid, succinic acid and sebacic acid on the ability to form microcapsules. Microencapsulation consisted in obtaining microcapsules with the core as well as without the core using the emulsion-coacervation method. The emulsion stabilizer was poly(vinyl alcohol) and the solvent for the polymer was chloroform. PBS-buffered solution and deionized water were used as non-solvents. Different mixing times of capsules without a core were used, and then the most favorable parameters were obtained with capsules with different filling. The obtained microcapsules were subjected to observations under a microscope.

2 Experimental Part

2.1 Material Synthesis

To create the microcapsules used are aliphatic copolyesters containing poly(butylene succinate) (PBSu) and poly(butylene sebacate) (PBSe) with different content of dimerized linoleic fatty acid (DLA). These types of copolymers have a multiblock structure, where the hard blocks are formed by succinates or sebacates sequences, while the soft blocks are formed by the butylene esters of the dimerized fatty acid. The polymers were obtained by polycondensation in the melt [8].

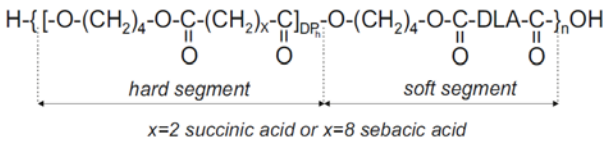

Fig. 1. Chemical structure of copolymers

West Pomeranian University of Technology in Szczecin, Polymer Institute, Division of Functional Materials and Biomaterials, Nanotechnology Centre, 45 Piastów Ave, Szczecin 70-311, Poland, agak@zut.edu.pl

TABLE 1
COPOLYMERS USED FOR THE PRODUCTION OF MICROCAPSULES

Copolymer	Hard segment content wt. %	Soft segment content wt. %
Copolyester based on succinic acid PBSu/DLA	100	0
	80	20
	50	50
Copolyester based on sebacic acid PBSe/DLA	100	0
	80	20
	50	50

As a result of the conducted syntheses, copolymers with variable weight shares of hard and soft blocks (Table 1) with the structure shown in Fig. 1 were obtained.

2.2 Microencapsulation

Microcapsules were obtained by coacervation method [9], both without and with the core. The production of the microcapsules with the filling proceeded in a similar way as without filling. As casing, copolyesters with different weight ratios were used, and as a filling - vitamins A and E and rape, argan and paraffin oils.

In a beaker with a magnetic stirrer, 48 ml of phosphate buffer solution (PBS) with 2 g poly(vinyl alcohol) PVA are mixed. To the solution using a burette, 1 g of polymer dissolved in 7 ml of chloroform ($CHCl_3$) was added dropwise. After 5 minutes of stirring, 187 ml of distilled water was added and further mixing was carried out. Fig. 2 presents the method of obtaining microcapsules.

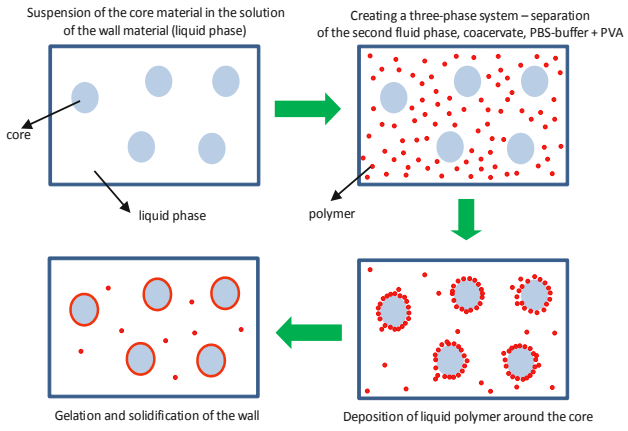

Fig. 2. Stages of microcapsule formation

3 RESULTS

The first stage of the research was to determine the influence of mixing time during formation on the quality of the emerging microcapsules. The obtained microcapsules were observed on a polarization-interference microscope (Fig. 3, Table 2). Microcapsules obtained from sebacic acid-based polymers were relatively easy to form, in contrast to polysuccinate capsules.

Even after 1.5 hours of mixing, precipitation of microcapsules could be observed, but they were characterized by a deformed spherical shape. With the increase polysebacate content in the copolyester it was easier to obtain a stable microcapsule with short mixing times.

Mixing time not only affects the size and formation of microcapsules, but also the surface structure of the microcapsule. It has also been observed that with short mixing processes, cracks occur on microcapsules, and the resulting microcapsules are deformed. The prolongation of the mixing time significantly improved the shape and structure of the microcapsule.

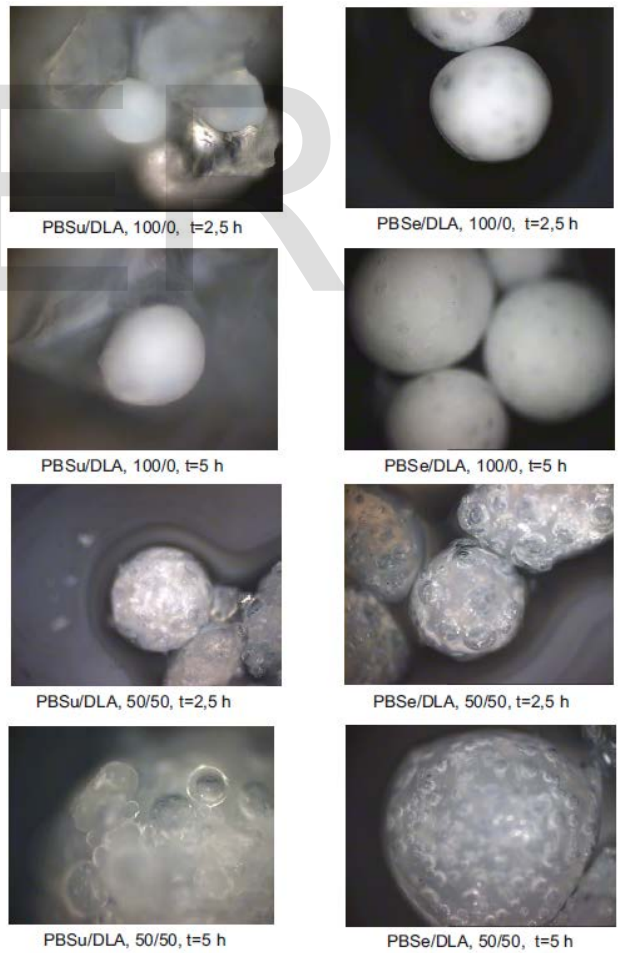

Fig. 3. Images from the polarization microscope of microcapsules depending on the time of mixing.

Based on the results of the conducted research on the preparation of polymeric microcapsules, it was observed that in addition to the significant influence of the mixing time on their size and shape, the core was also used.

The best capsules were created when vitamin A was used as the core. In the trials with oils, i.e. paraffin, argan oil or vegetable oil using polysuccinate, regardless of the proportion of dimerized fatty acid in the macromolecule, most often no microspheres were formed or formed and were significantly deformed.

In the case of polymers with PBSe during microencapsulation, much better results were obtained irrespective of the weight fraction of the soft DLA segment. Almost all tested substances were closed in capsules except vitamin E, which could be caused by too high a density of the immobilized substance.

With the use of paraffin oil, clear microcapsules of regular shape for pure PBSe (Fig. 4) have emerged from its small amount.

TABLE 2
PARAMETERS OF FORMATION OF MICROCAPSULES WITHOUT CORE - PVA STABILIZER 4% , MIXING SPEED OF 1200 RPM

Copolymer	Mixing time [h]	Results
PBSu/DLA 100/0	1,5	-
	2	-
	2,5	+
	5	+
PBSu/DLA 80/20	1,5	-
	2	-
	2,5	+
	5	+
PBSu/DLA 50/50	1,5	-
	2	-/+
	2,5	+
	5	+
PBSe/DLA 100/0	1,5	-/+
	2	+
	2,5	+
	5	+
PBSe/DLA 80/20	1,5	-/+
	2	+
	2,5	+
	5	+
PBSe/DLA 50/50	1,5	-
	2	+
	2,5	+
	5	+

When using the vitamin A as core, in each case of the poly(butylene sebacate), regardless of the participation of DLA, microspheres were formed. However, it can be noted that as the soft segment of DLA grew, the microcapsules became more spherical, their shapes became more and more regular. As you can see in the pictures below, you can see this difference (Fig. 4).

TABLE 3
PARAMETERS OF FORMATION OF MICROCAPSULES WITH CORE - PVA STABILIZER 4% , MIXINGTIME 5 H, SPEED OF 1200 RPM

Copolymer	Core	Amount of used filling [g]	Results
PBSu/DLA 100/0	Rape oil	11,26	-
	Paraffin oil	13,06	-
	Argan oil	10,39	-
	Vitamin E	12,55	-
	Vitamin A	14,24	+
PBSu/DLA 80/20	Rape oil	10,56	-
	Paraffin oil	13,25	-
	Argan oil	10,01	-/+
	Vitamin E	11,25	-
	Vitamin A	10,02	+
PBSu/DLA 50/50	Rape oil	12,98	-/+
	Paraffin oil	13,26	-
	Argan oil	13,11	-/+
	Vitamin E	12,03	-
	Vitamin A	11,24	+
PBSe/DLA 100/0	Rape oil	10,24	-/+
	Paraffin oil	13,46	+
	Argan oil	13,11	+
	Vitamin E	10,39	-
	Vitamin A	12,01	+
PBSe/DLA 80/20	Rape oil	12,77	-/+
	Paraffin oil	11,44	+
	Argan oil	12,99	+
	Vitamin E	10,02	-
	Vitamin A	13,21	+
PBSe/DLA 50/50	Rape oil	12,77	-/+
	Paraffin oil	10,40	-/+
	Argan oil	12,99	+
	Vitamin E	10,35	-
	Vitamin A	10,43	+

4 CONCLUSION

The work presents the method of obtaining polymeric microcapsules. The effect of the composition of the copolymer used, the mixing time and the type of fill used on the obtained microcapsules were investigated.

In the case of both series of polymers containing varying amounts of dimerized fatty acid butylenes, the copolyesters used have lower or higher capability to obtain microcapsules. However, much better properties for the preparation of microcapsules are demonstrated by the sebacic acid copolyester, regardless of the weight ratio of the dimerized fatty acid.

The results presented in the study are significant from a cognitive and practical point of view. New biodegradable polyester copolymers can be used primarily in pharmacy and medicine as DDS.

Fig. 4. Images from polarization microscope microcapsules with different filling.

REFERENCES

[1] Smażyński T.: Mikrokapsułkowanie, Państwowy Zakład Wydawnictw Lekarskich, Warszawa 1981;
[2] Bartkowiak A., Brylak W.: Polimery 2006, **51**, 547 – 554;
[3] Jadupati M., Tanmay D., Souvik G.: Microencapsulation: an indispensable technology for drug delivery system, International Research Journal of Pharmacy 2012, **3**, 8 – 13;
[4] Rathore S. et al.: Microencapsulation of microbial cells. Journal of Food Engineering, v.116, n.2, p.369-381, 2013;
[5] Saralidze K., Koole L.H., Knetsch M.L.W.: Polymeric Microspheres for Medical Applications, Materials 2010, **3**, 3537 – 3564;
[6] Benita S.: Microencapsulation. Methods and Industrial Applications, Taylor and Francis Group, New York 2006;
[7] Nack H.: Microencapsulation Techniques, Applications and Problems, J.Soc. Cosmetic Chemists 1970, **21**, 85 – 98;
[8] Kozłowska A.:, Elastomery 2008 t.12, 1, 15 – 19;
[9] Kozłowska A.: Przetwórstwo Tworzyw 2011, 5, 324 – 326