P-048 The influence of type and molecular mass of polyquaternium polymers on mechanical properties of binary polyelectrolyte capsules.

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INTRODUCTION AND OBJECTIVES

One of the main disadvantages of the classic alginate/Ca^{2+} microcapsules is its low mechanical resistance and stability, which occur during their storage in typical buffer solution containing monovalent metal cations and multivalent anions. To overcome this problem the use of additional coating by polycation or direct reaction with it instead of gelation by multivalent ions, has been proposed over the last two decades in many patents and publications.

There are many parameters, which have the direct impact on the formation of stable membrane at the interface between the drop of polyanion (e.g. alginate) and cationic polymer in hardening solution. Among these parameters, molecular mass of polycation seems to be one of the most important, since it influences the polymer diffusion parameters during formation of mechanically stable membrane (Prokop et al. 1998).

Polyquaterniums are a family of synthetic, cationic polyelectrolytes with different chemical structure, commonly used in cosmetics industry (Tab.1)

The main objective of this work was to investigate the influence of molecular mass of selected water-soluble cationic polymers from the group of polyquaterniums on the mechanical strength of binary polyelectrolyte capsules using four different natural anionic polysaccharides.

Table 1: Chemical composition of polyquaterniums

Polyquat. 5	4% methacryloyloxethyl trimethyl ammonium methylsulfate, 96% acrylamide
Polyquat. 6	homopolymer DADMAC
Polyquat. 7	30% DADMAC, 70% acrylamide
Polyquat. 39	35% Acrylic acid, 30% DADMAC, 35% acrylamide
Polyquat. 47	46% acrylic acid, 46% aethacrylamidopropyltrimethylammonium chloride, 8% acrylamide
Polyquat. 53	10% acrylic acid, 40% methacrylamidopropyltrimethylammonium chloride, 50% acrylamide

MATERIALS AND METHODS

Polyanions: alginate, pectin and iota-carrageenan were purchased from Sigma. Cellulose sulphate was from ACROS (Belgium) and calcium chloride was from Chempur (Poland). All six polyquaternium polycations (Table 1) were a gift from Nalco (USA).
In the experiment 5ml of specific 1% polyanion were added dropwise into 100 ml of selected 0,5% polyquat.
If the precipitation did not occur, capsules were allowed to stay in the gelling bath for 30 minutes. After that they were washed in distilled water for another half an hour before mechanical strength tests were performed. Ten capsules per batch were analyzed in order to obtain statistically relevant data.

To estimate the influence of molecular mass decrease on the formation of membrane, two polyquaterniums (7 and 53) were depolymerised using ultrasound generator (UP400S, Hielscher, Germany) 0,5 cycle at 80% amplitude. This method of degradation has been chosen, since it should not affect the chemical structure of the cationic polymer (Szu et al. 1986). Samples after depolymerisation were diluted, filtered (0,22µm) and injected (10µl) into a liquid chromatograph HPLC (Knauer, Germany) equipped with RI detector. Dextran standards (PSS, Germany) were used to calibrate GPC column (PSS NOVEMA 3000Å, Germany) heated to 30°C. As HPLC eluent aqueous 0,9% NaCl at a flow rate of 1 mL/min has been applied.

To investigate stability in the culture medium three types of following capsule were prepared:
- alginate/Ca capsules prepared by drop-extruding 5mL of 1% alginate into a 100 mL of 0,155M $CaCl_2$.,
- carrageenan/Polyquat. 53 (sonodegradated for 4 hours) capsules obtain in similar method like previous one.
- (alginate/carrageenan)/Ca/Polyquaternium capsules a mixture of 1% alginate/1% iota-carrageenan has been used as polyanion gelled in a mixture of 0,5% Polyquaternium 53 (4h sonodegradation; LMW)/0,155M $CaCl_2$ solution. After formation capsules were transferred into a culture medium used typically in biological conversion of glycerol to diols or dicarboxylic acids (project No 01.01.02-00-074/09) based on mixtures of K_2HPO_4, KH_2PO_4, $(NH_4)_2SO_4$, $MgSO_4$*7H_2O salts with yeast extract bacto-peptone and bacteriological meat extract stabilised with 1g/l of sodium azide to avoid bacteria growth. Mechanical strength tests, as an indicator of capsules stability, were performed after 12 and 24 hours.

RESULTS AND DISCUSSION

In most experiments polyanion-polycation surface complex formation result in spontaneous precipitation. Especially in case of two polysaccharides: alginate and pectin, which are polymers with weak carboxyl functional group, no integral polyelectrolyte membrane could be achieved. On the contrary to these results, sulfated polysaccharides, having strong anionic $–SO_3$ groups, have formed membrane on the surface of polyanion drop. Although, some of these capsules precipitate during the gelling (CP- capsule precipitation), the rest of them formed weak membrane (WM), which was destroyed during the attempts to take them out from the polycation solution. In two cases the membrane did not broke up, but the capsules have low mechanical strength (WC) (Tab. 2). Since the best results in this preliminary study were obtain for carrageenan and Polyquaternium 7 and 53, these two systems have been choose to investigate the influence of molecular mass on the formation of more stable membrane.

Table 2: Type of polyelectrolyte complex formation process by each of the cationic polyquaterniums with different polyanions.

Polycation	Polyanion			
	Alginate	Pectin	Cellulose sulphate	Carrageenan
Polyquat. 5	P	P	P	P
Polyquat. 6	P	P	WM	WM
Polyquat. 7	P	P	CP	**WC**
Polyquat. 39	P	P	P	P
Polyquat. 47	P	P	CP	WM
Polyquat. 53	P	P	WM	**WC**

P- precipitation, CP- capsule precipitation, WM- weak membrane, WC- weak capsule.

Application of ultrasounds has allowed to decrease molecular mass of both cationic polymers. In case of polyquaterium 7 one can observe some increase in mechanically resistance already after 0,5 hour of degradation, where there was no further significant increase with prolongation of sonification time.
For sample of polyquaternium 53 degradated for four hours one can observe the significant increase (more than 6x) in capsule mechanical resistance (Tab. 3).

Table 3: The influence of ultrasound depolymerisation on the molecular mass of polycations and mechanical strength of carrageenan capsules.

Duration of ultrasound treatment	**Molecular mass (g/mol)**		**Mechanical strength [N]**
	M_w	M_n	
Polyquaternium 7			
0 h	10 460 000	170 000	0,13±0,02
0,5 h	224 000	72 000	0,31±0,06
1 h	169 000	66 000	0,32±0,06
2 h	152 000	65 000	0,32±0,04
4 h	105 000	50 000	0,41±0,08
Polyquaternium 53			
0 h	1 305 000	86 000	0,09±0,04
0,5 h	220 000	51 000	0,07±0,02
1 h	160 000	48 000	0,09±0,02
2 h	118 000	44 000	0,10±0,02
4 h	100 000	42 000	0,58±0,08

In the stability experiments three types of capsules based on polyquaternium 53 (ultrasound-treated for 4 hours) were transferred into the culture medium solution and incubated for 12 and 24 hours (Tab. 4).

A standard alginate/Ca-based capsules after 12h shown severe decrease in mechanical resistance, as well as its integrity, which indicate that alginate/calcium complex was destroyed. Similar results were obtained for capsules prepared using the alginate/carrageenan mixture.

Table 4: Mechanical resistance of capsules after storage in culture medium.

Capsule type	Bursting strength [N] after incubation for		
	0h	12h	24h
$Alginate/Ca^{2+}$	1,52 ±0,12	*	*
Iota-Carrageenan/ Polyquaternium 53 (LMW)	0,58 ±0,08	0,10 ±0,02	0,06 ±0,02
Alginate/Carrageenan/ Polyquaternium 53 (LMW)/Ca^{2+}	0,48 ±0,09	0,09 ±0,01	0,08 ±0,02

* Capsules have lost their integrity
LMW- low molecular weight, sono-degradation for 4 hours.

CONCLUSIONS

The present study indicated that by controlled decreasing of molecular mass of preselected cationic polymers one can enhance the mechanical stability of both types of polyelectrolyte capsules including binary (Dautzenberg type) and multicomponent ones (Vanderbillt type).
More process parameters (e.g. concentration, temperature, pH, etc.) along with properties of final microcapsules, must be further investigate before any final conclusions, about potential application of polyquaterniums in PEC capsule preparation principles, can be made.

REFERENCES

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