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A new foaming technique for production of superabsorbents from carboxymethyl chitosan

Akram Zamani [a,b,*], Dag Henriksson [a], Mohammad J. Taherzadeh [a]

[a] School of Engineering, University of Borås, 50190 Borås, Sweden
[b] Department of Chemical and Biological Engineering, Chalmers University of Technology, 41296 Göteborg, Sweden

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ABSTRACT

A foaming technique was developed for production of superabsorbent polymers (SAP) from carboxymethyl chitosan (CMCS) with high, medium and low molecular weights. In this method *n*-pentane was used as a blowing agent due to low boiling point and immiscibility with water. *n*-Pentane was added to a warm aqueous solution of CMCS and boiled. CMCS was then gelled by adding the crosslinking agent glutaraldehyde and consequently *n*-pentane was captured inside the polymer network. The *n*-pentane was evaporated from this network while drying in oven. It resulted in stable foam that prevented the hydrogel from collapsing and the dried product had a porous structure with a high water-binding capacity (WBC). The effects of molecular weight of CMCS and its concentration, and the amounts of glutaraldehyde and *n*-pentane used, on WBC were investigated and optimized using response surface experimental design. The best result for WBC of foam-dried SAP was 107 (g/g) after exposing for 1 h in pure water and 60 (g/g) and 37 (g/g) after exposing for one min in pure water and 0.9% NaCl solution, respectively. The WBC of the SAP produced by the foaming technique was more than five times higher than the WBC of the oven-dried crosslinked CMCS.

1. Introduction

Superabsorbent polymers (SAP) are highly hydrophilic polymer networks which are three-dimensionally crosslinked and able to swell, absorb and retain water up to a 100 times their dry weight. They are nowadays widely used in personal care and hygienic products (Hongmei Kang, 2003; Kabiri, Omidian, Hashemi, & Zohuriaan-Mehr, 2003a; Li, Zhang, & Wang, 2007; Zhang, Li, & Wang, 2006). Crosslinked polymers of acrylic acid are the most common materials for production of SAP, resulting in a high water-binding capacity (WBC) and water-binding rate (WBR), even under load (Buchholz & Graham, 1998; Dutkiewicz, 2002). Nevertheless, in recent years attention has been paid to applying biodegradable materials such as cellulose and starch for disposable medical articles and personal care products in order to reduce waste problems. However, these materials do not have good WBC compared to polyacrylates. Therefore, it is necessary to convert them to more hydrophilic materials by e.g. carboxymethylation. Carboxymethyl cellulose and carboxymethyl starch have been successfully used for production of superabsorbents (Dutkiewicz, 2002; Li et al., 2007).

Polyacrylates and carboxymethylated cellulose and starch are anionic polymers with high WBC at neutral and basic pH. The human skin is slightly acidic with pH 4.3–6.6 at which the WBC of the anionic SAPs is to some extent decreased (Dutkiewicz, 2002; Ehlers, Ivens, Moller, Senderovitz, & Serup, 2001; El-Rehim, Hegazy, & El-Mohdy, 2006; Hongmei Kang, 2003; Waller & Maibach, 2005), while polycationic SAPs show better performance (Chen, Tian, & Du, 2004; Dutkiewicz, 2002).

Chitosan is a cationic polysaccharide that is produced by deacetylation of chitin. It is soluble at acidic pH and can be crosslinked and converted to SAP. The WBC of SAP from pure chitosan has been reported up to 85 g water/g SAP for pure water and 25 g/g for 0.9% NaCl solution under 2.1 kPa load (Dutkiewicz, 2002). However, the poor solubility of chitosan in pure water is the major limiting factor for its applications (Lu, Song, Cao, Chen, & Yao, 2004). Carboxymethyl chitosan (CMCS) is a well-known water-soluble derivative of chitosan (Chen & Park, 2003; Liu, Guan, Yang, Li, & De Yao, 2001; Muzzarelli, 1988; Wang L. & Wang, A., 2008; Zhuang & Liu, 2006). It has been reported that CMCS hydrogels have improved WBC at pH > 4 and can be used as drug carriers with controlled release (Chen & Park, 2003). However, there is little attention to the production of SAP from CMCS. Our preliminary experiments showed that this might be due to shrinkage of crosslinked CMCS during the oven-drying, which reduces the WBR significantly. Freeze-drying is a suitable method to avoid the

* Corresponding author. Address: School of Engineering, University of Borås, 50190 Borås, Sweden. Tel.: +46 33 4354360; fax: +46 33 4354008.
E-mail address: akram.zamani@hb.se (A. Zamani).

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Nomenclature

CMCS	carboxymethyl chitosan	SAP	superabsorbent polymers
CRC	centrifuge retention capacity	WBC	water-binding capacity
Mw	molecular weight	WBR	water-binding rate

shrinkage of the materials during the drying. However, it is an expensive drying method.

The WBR of SAP can be improved by generation of a superporous structure. This structure is formed by using phase separation, porosigen and foaming techniques (Kabiri et al., 2003a). In the latter technique, porosity of SAP is achieved by generation of gas bubbles during the polymerization and crosslinking. Sodium bicarbonate is a known blowing agent which produces CO_2 bubbles at acidic pH. Acetone, which is a low boiling point liquid, is also a good porosity generator (Kabiri et al., 2003a; Kabiri, Omidian, & Zohuriaan-Mehr, 2003b; Kiatkamjornwong & Wongwatthanasatien, 2001; Omidian, Rocca, & Park, 2005). Water-insoluble liquids with a low boiling point such as alkanes with 5–7 carbon atoms are other examples of blowing agents (Phan, 1994), for example *n*-pentane which boils at 36 °C. We have used different blowing agents for production of SAP from CMCS in our preliminary experiments and among them, *n*-pentane showed an improved WBC and WBR of crosslinked CMCS and became the basis of the current study.

The goal of this work was to develop a new foaming technique for production of SAPs from CMCS with a porous structure that have high WBC and WBR. This was achieved by using *n*-pentane as the blowing agent. The new method was then applied to carboxymethylated derivative of three commercial samples of shrimp-based chitosan with different molecular weights (high, medium and low). Response surface design was used to obtain the optimum condition for production of SAP from each CMCS that gave the highest WBC. The WBCs of the products in pure water and salt solution were compared with two reference drying methods, i.e. freeze-drying and oven-drying.

2. Materials and methods

2.1. Materials

Three commercial shellfish chitosans (Aldrich) of (a) low molecular weight with 20 cP viscosity (1% solution in 1% acetic acid), (b) medium molecular weight with 200 cP viscosity and (c) high molecular weight with 800 cP viscosity were used in this work. The degree of deacetylation (DD) of those chitosans was 0.827, 0.836 and 0.931 (mol/mol), respectively (Zamani, Jeihanipour, Edebo, Niklasson, & Taherzadeh, 2008). Two commercial synthetic superabsorbents, Sumitomo 5EIKA (5A70) and Aqualic ca (L520) were used in this work as reference SAP, and the WBCs of the products were compared to their WBCs.

2.2. Carboxymethylation of chitosan

Carboxymethyl chitosan, CMCS was prepared according to the method presented by Pang, Chen, Park, Cha, and Kennedy (2007) with minor modifications. Briefly, one gram chitosan was mixed with 1.35 g powdered sodium hydroxide, followed by addition of 8 ml 2-propanol and 2 ml water. It was then mixed with a solution containing 1.5 g monochloroacetic acid in 2 ml 2-propanol. The carboxymethylation reaction of the chitosan occurred in 4 h, while the chitosan mixture was mixed at 200 rpm at room temperature. The reaction was then stopped by adding 50 ml 70% ethanol to the mixture and carboxymethyl chitosan was separated by filtration. It was washed four times with 70% ethanol to desalt and dewater and dried at 50 °C. The product was the sodium salt of CMCS.

2.3. Characterization of carboxymethyl chitosan by FTIR

The sodium salt of CMCS (1 g) was converted to acid form by immersing in 70% ethanol (100 ml) and adding hydrochloric acid (10 ml, 32%). The resultant suspension was mixed for 30 min and then was filtered and washed with 70% ethanol and dried. The product was the acid form of CMCS (Chen & Park, 2003). It was subjected directly to FTIR analysis with a DuraSample IR (SensIR Technologies, Danbury, CT, USA) instrument.

2.4. Measurement of degree of substitution (Ds)

Degree of substitution (Ds), which is the relative number of carboxymethylated groups in the chitosan chain, was measured with the conductimetric method (Campana-Filho, 2005; Capitani, Porro, & Segre, 2000). About 0.1 g of CMCS was dissolved in 100 ml of 0.05 M HCl and the pH was increased to 2.0–2.2 by adding 0.1 M NaOH. It was then titrated with 0.1 M NaOH up to pH 11.5. The typical titration curve is shown in Fig. 2 and the Ds was measured according to the following equation:

$$\mathrm{Ds} = \frac{(V_2 - V_1) \times \mathrm{DD}}{(V_3 - V_2)} \quad (1)$$

where Ds is the degree of substitution of CMCS (mol/mol of total monomers) and DD is the degree of deacetylation of the original chitosan.

2.5. Preparation of SAPs from CMCS

The produced CMCS was crosslinked in aqueous media by using glutaraldehyde as the crosslinking agent and dried with different methods including freeze-drying, oven-drying and oven-drying in combination with the foaming technique. For all of the drying methods, CMCS was first dissolved in distilled water to known concentrations. It was then preheated in a water bath to 60 °C. For the freeze-drying and the ordinary oven-drying, 0.02–0.08 (g glutaraldehyde/g CMCS) was added to the carboxymethyl chitosan solution (cf. Table 1). The solution was then mixed with a homogenizer at 25,000 rpm for 30 s. CMCS gel was formed in less than 5 min which was either dried in an oven at 60 °C or frozen and freeze-dried (Labconco, USA).

The drying by the foaming technique was applied using *n*-pentane as the blowing agent in order to create a porous structure of CMCS. A known amount of *n*-pentane was added to the preheated CMCS solutions and mixed at 25,000 rpm for 30 s to disperse the blowing agent in the polymer solution. Then, 0.012–0.06 (g glutaraldehyde/g CMCS) was added to the mixture and this was homogenized for another 30 s (cf. Tables 2–4). The obtained CMCS gel was subsequently dried in an oven equipped with a fan at 60 °C.

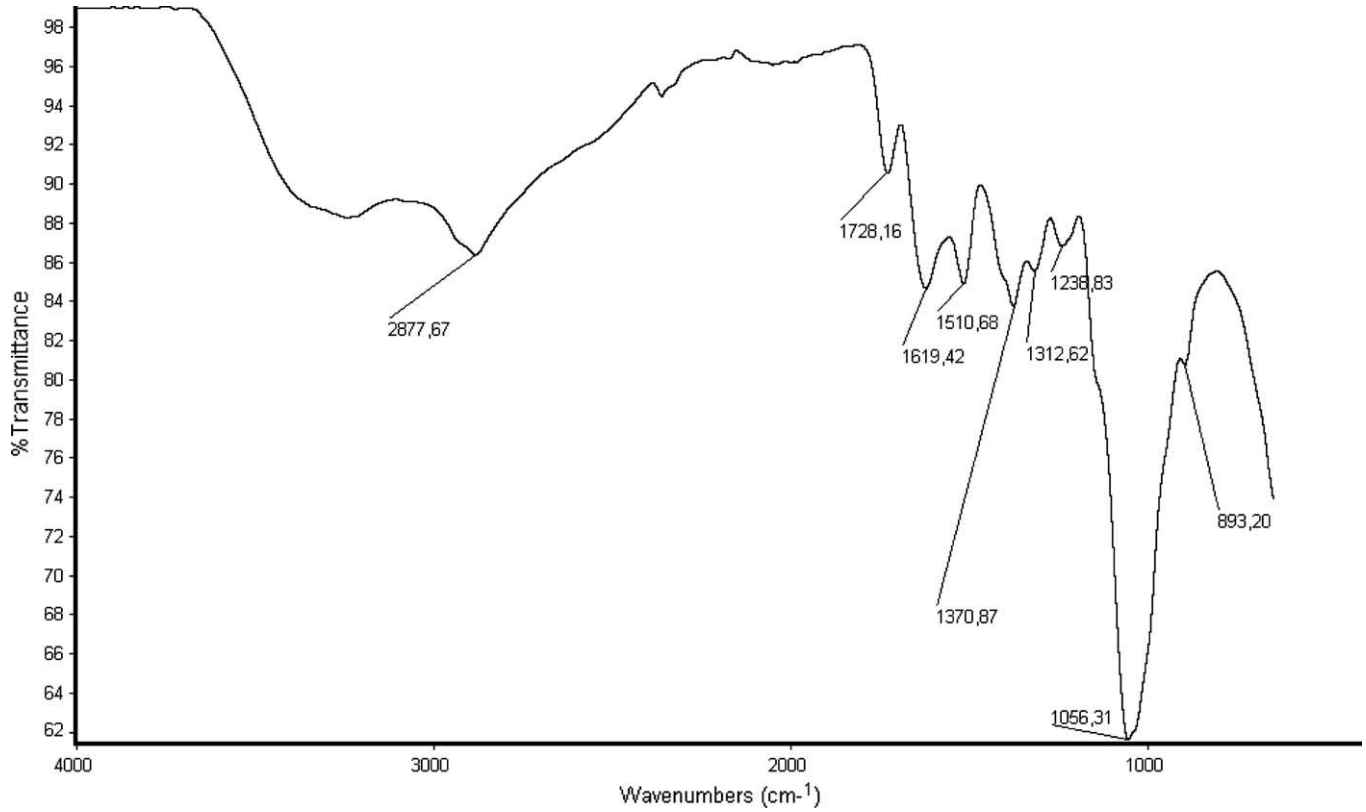

Fig. 1. The FTIR spectrum of low Mw carboxymethyl chitosan (the spectra of carboxymethyl chitosan with low, medium and high Mw were similar).

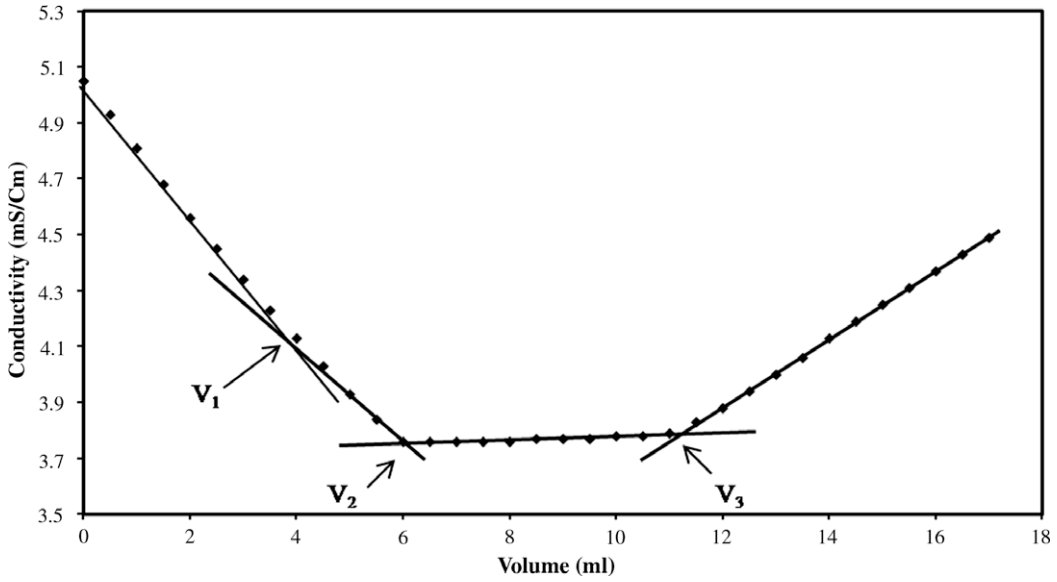

Fig. 2. Typical conductimetric titration curve of solution of carboxymethyl chitosan in HCl titrated with sodium hydroxide solution (conductivity vs. sodium hydroxide volume).

2.6. Measurement of the water-binding capacity (WBC) and the Centrifuge Retention Capacity (CRC)

The dried crosslinked CMCSs were cut to small particles (less than 1 mm) by using a coffee grinder and their WBCs were measured after immersing in distilled water and 0.9% NaCl solution. For this purpose, 0.025–0.050 g of the samples was put in a small bag made of nonwoven materials and the bag was immersed in the water/salt solution for a specific period of time (1 and 60 min for pure water and 1 min for salt solution). Then, the swollen absorbent gel was collected with a spatula from the bag and weighed. The absorbency of the samples was measured according to the following equation:

$$\mathrm{WBC} = \frac{W_2 - W_1}{W_1} \tag{2}$$

Table 1
Water absorbency of freeze-dried and oven-dried crosslinked CMCS and two commercial polyacrylate-based SAPs.

SAP[1]	Drying method	Glutaraldehyde (g/g)[2]	Absorbency after different exposure times (g/g)			
			Water 1 min	Water 60 min	Salt solution[3] 1 min	CRC[4] 60 min
High-Mw	Freeze-drying	0.04	67	173	35	122
High-Mw	Freeze-drying	0.02	73	143	45	150
High-Mw	Oven-drying	0.04	11	7	16	9
High-Mw	Oven-drying	0.02	11	7	33	24
Med-Mw	Freeze-drying	0.04	54	176	45	105
Med-Mw	Freeze-drying	0.02	81	134	43	135
Med-Mw	Oven-drying	0.04	18	12	26	21
Med-Mw	Oven-drying	0.02	9	8	18	12
Low-Mw	Freeze-drying	0.08	44	83	32	49
Low-Mw	Freeze-drying	0.04	58	108	38	64
Low-Mw	Oven-drying	0.08	5	2	7	10
Low-Mw	Oven-drying	0.04	5	6	8	8
L520[5]	–	–	63	285	23	241
5A70[6]	–	–	158	579	28	415

[1] Concentration of CMCS was 1%.
[2] g glutaraldehyde per g of CMCS.
[3] 0.9% sodium chloride solution.
[4] Centrifuge Retention Capacity in water.
[5] Sumitomo 5EIKA, a commercial synthetic superabsorbent.
[6] Aqualic ca, a commercial synthetic superabsorbent.

Table 2
Uncoded (real) levels of the three variables, i.e. the amount of glutaraldehyde, *n*-pentane and the "high" Mw CMCS concentration and their response factor (WBC) of the foam-dried CMCS.

Glutaraldehyde (g/g)[1]	*n*-Pentane (ml/ml)[2]	Concentration (%)	Absorbency after different exposure times (g/g)			
			Water 1 min	Salt solution[3] 1 min	Water 60 min	CRC[4] 60 min
0.015	0.62	1.70	45	34	82	48
0.020	0.50	2.00	60	33	80	58
0.012	0.50	2.00	59	30	74	57
0.025	0.38	1.70	39	30	61	45
0.020	0.50	2.00	50	35	75	67
0.015	0.62	2.30	56	34	75	68
0.020	0.50	1.50	60	37	88	59
0.020	0.30	2.00	35	28	57	48
0.015	0.38	1.70	50	30	60	66
0.020	0.50	2.50	45	27	68	45
0.020	0.70	2.00	46	25	75	68
0.020	0.50	2.00	51	32	94	64
0.020	0.50	2.00	58	31	85	68
0.025	0.38	2.30	40	27	57	37
0.025	0.62	1.70	55	32	93	75
0.020	0.50	2.00	49	28	90	72
0.015	0.38	2.30	44	27	77	44
0.025	0.62	2.30	33	18	55	46
0.028	0.50	2.00	38	20	56	41
0.020	0.50	2.00	56	30	87	66

[1] g glutaraldehyde per g of CMCS.
[2] ml of *n*-pentane per ml of CMCS solution.
[3] 0.9% sodium chloride solution.
[4] Centrifuge Retention Capacity in water.

where WBC is the absorbency of the sample (g absorbed liquid per g of absorbent material), W_1 is the dry weight of the absorbent and W_2 is the final weight of the swollen gel. The same procedure was followed for the CRC measurement. After immersing the bags for 1 h in distilled water, they were taken from the water and placed in 50 ml Vivaspin filter tubes (Sartorius Biolab products, Germany) and centrifuged for 3 min at 240*g*. The swollen gels were then collected from the bags and weighed and CRC was calculated according to Eq. (2) by replacing the WBC with the CRC.

2.7. Statistical analysis

The response surface design (the central composite design) was used to investigate the effect of three different variables, i.e. the amount of glutaraldehyde (g), the amount of *n*-pentane (p) and the concentration of CMCS (c), on the WBC and CRC of the foam-dried CMCSs with different molecular weights. The type and the range of the variables were selected based on 10 preliminary experiments on each CMCS (data not shown). MINITAB® package was used for design of the tests and also evaluation of the results. The number of experiments in central composite design is the sum of 2^k factorial runs, $2k$ axial runs and the number of replicates in the center point. We had three factors and the recommended number of replicates in the center was six; hence the total number of tests for each CMCS was 20. The uncoded levels of the three variables for different CMCSs are presented in Tables 2–4. A second-order polynomial equation was chosen to model the effect of the factors:

Table 3
Uncoded (real) levels of the three variables, i.e. the amount of glutaraldehyde, *n*-pentane and the "medium" Mw CMCS concentration and their response factor (WBC) of the foam-dried CMCS.

Glutaraldehyde (g/g)[1]	*n*-Pentane (ml/ml)[2]	Concentration (%)	Absorbency after different exposure times (g/g)			
			Water 1 min	Salt solution[3] 1 min	Water 60 min	CRC[4] 60 min
0.015	0.62	1.70	48	37	90	70
0.020	0.50	2.00	52	28	81	70
0.012	0.50	2.00	60	31	96	70
0.025	0.38	1.70	33	25	80	70
0.020	0.50	2.00	55	30	80	48
0.015	0.62	2.30	43	28	100	66
0.020	0.50	1.50	24	33	107	60
0.020	0.30	2.00	34	24	59	40
0.015	0.38	1.70	29	26	83	53
0.020	0.50	2.50	27	24	51	42
0.020	0.70	2.00	49	32	85	69
0.020	0.50	2.00	51	32	98	62
0.020	0.50	2.00	51	35	101	74
0.025	0.38	2.30	40	30	64	48
0.025	0.62	1.70	56	30	102	75
0.020	0.50	2.00	56	37	106	74
0.015	0.38	2.30	29	24	57	33
0.025	0.62	2.30	38	26	93	74
0.028	0.50	2.00	49	31	91	63
0.020	0.50	2.00	50	33	80	66

[1] g glutaraldehyde per g of CMCS.
[2] ml of *n*-pentane per ml of CMCS solution.
[3] 0.9% sodium chloride solution.
[4] Centrifuge Retention Capacity in water.

Table 4
Uncoded (real) levels of the three variables, i.e. the amount of glutaraldehyde, *n*-pentane and the "low" Mw CMCS concentration and their response factor (WBC) of the foam-dried CMCS.

Glutaraldehyde (g/g)[1]	*n*-Pentane (ml/ml)[2]	Concentration (%)	Absorbency after different exposure times (g/g)			
			Water 1 min	Salt solution[3] 1 min	Water 60 min	CRC[4] 60 min
0.028	0.62	1.41	13	7	55	26
0.040	0.50	2.00	30	20	59	49
0.020	0.50	2.00	25	28	72	49
0.052	0.38	1.41	20	15	30	23
0.040	0.50	2.00	28	20	56	52
0.028	0.62	2.60	33	24	65	61
0.040	0.50	1.00	7	6	15	34
0.040	0.30	2.00	20	14	38	27
0.028	0.38	1.40	7	8	55	17
0.040	0.50	3.00	23	19	45	31
0.040	0.70	2.00	24	19	55	42
0.040	0.50	2.00	28	21	62	44
0.040	0.50	2.00	27	22	66	45
0.052	0.38	2.60	26	21	36	29
0.052	0.62	1.41	33	31	80	51
0.040	0.50	2.00	28	28	63	43
0.028	0.38	2.60	25	23	31	36
0.052	0.62	2.60	18	13	24	17
0.060	0.50	2.00	20	19	29	29
0.040	0.50	2.00	38	25	82	34

[1] g glutaraldehyde per g of CMCS.
[2] ml of *n*-pentane per ml of CMCS solution.
[3] 0.9% sodium chloride solution.
[4] Centrifuge Retention Capacity in water.

$$\text{Absorbency} = b_0 + b_1 g + b_2 p + b_3 c + b_{11} g^2 + b_{22} p^2 + b_{33} c^2 + b_{12} gp + b_{13} gc + b_{23} pc + e \quad (3)$$

where g, p and c are the amounts of glutaraldehyde and *n*-pentane and the concentration, respectively, and b_i, b_{ii} and b_{ij} are the coefficients of the equations which were determined based on the results by regression analysis using the least-squares method. For *p*-values higher than 0.05 at 95% confidence level, the effects were considered not to be statistically significant. The optimal production condition for each CMCS was obtained from the response surface contour plots.

3. Results

3.1. Preparation and characterization of carboxymethyl chitosan (CMCS)

When CMCS is produced with monochloroacetic acid, the carboxymethylation of chitosan may occur on both $-NH_2$ and –OH

positions, where the resulting products are called *N*-carboxymethyl and *O*-carboxymethyl chitosan, respectively (Muzzarelli, 1988). It is therefore important to measure the proportion of these groups in the CMCS chains. For this purpose, FTIR and the conductimetric titration were used for characterization of the CMCS.

The FTIR spectra of different CMCSs synthesized in this work were similar to the spectrum of low molecular weight chitosan which is shown in Fig. 1. The peak at 1728 cm^{-1} corresponds to the C=O stretching vibration and the peak at 1238 cm^{-1} represents the C–O stretching vibration bond of the group $–CH_2COOH$. These two peaks confirm the existence of carboxymethyl groups. The bonds at 1510 and 1619 cm^{-1} correspond to $–NH_3^+$ and indicate that the carboxymethyl groups are in –OH positions (Chen & Park, 2003; Zhuang & Liu, 2006). Degree of substitution (Ds), which is the ratio of carboxymethylated groups to the total number of monomers in the chitosan chain, was measured according to the conductimetric method (Campana-Filho, 2005; Capitani et al., 2000). A typical conductimetric titration curve of carboxymethyl chitosan consists of four linear branches (Fig. 2). The first branch (from 0 to V_1) corresponds to the volume of NaOH used for neutralization of the excess amount of HCl. The second one shows the volume reacted with the carboxymethyl groups (from V_1 to V_2). The third branch (from V_2 to V_3) is related to the NaOH added to react with the NH_3^+ groups of chitosan, and finally the last one (from V_3 to the end) is due to the excess amount of NaOH in the solution (Campana-Filho, 2005). We assumed that the degree of deacetylation (DD) of chitosan did not change during the carboxymethylation reaction. In Fig. 2, $V_3–V_2$ is proportional to the number of the glucosamine residues in the chitosan chain. Since $V_3–V_2$ is not dependent on the number of carboxymethylated groups, $(V_3–V_2)/DD$ is proportional to the number of building blocks of the polymer chains and the Ds can be calculated according to the Eq. (1). The calculated Ds of low, medium and high molecular weight CMCSs were 0.16, 0.29 and 0.27 (mol/mol), respectively.

3.2. Preparation of the SAP from CMCS

Production of the SAP was carried out by crosslinking of CMCSs in aqueous solutions and drying the obtained hydrogel. Glutaraldehyde was used as the crosslinking agent, while different methods of drying including freeze-drying, oven-drying and a combination of oven-drying and foaming technique were used to dry the SAP.

Among different drying methods, freeze-drying resulted in the highest WBC. Table 1 shows the absorbency of the freeze-dried products. The WBC of the SAPs after 60 min was 83–176 g/g, and 31–60% of this amount of water was absorbed within the first minute. The SAPs were able to keep 59–100% of the absorbed water under the force applied by centrifugation (CRC). On average, CMCS with low Mw had the best WBR, but the lowest WBC after 60 min as well. The amount of glutaraldehyde had a major effect on the water-binding properties. For chitosans with high and medium molecular weights, the water absorbency at 60 min was decreased by decreasing the amount of glutaraldehyde, while CRC and WBR were increased. For the low Mw chitosan, 0.04 (g glutaraldehyde/g CMCS) gave the best results. Adding the salt to water did not decrease the water absorbency significantly and all the SAPs were able to absorb 52–82% of absorbed water after 1 min in the presence of 0.9% NaCl (Table 1).

Oven-drying of all carboxymethyl chitosan samples in this work ended up with formation of a light brown film with poor WBC in comparison with the freeze-dried samples, regardless of the amount of glutaraldehyde added and the molecular weight of the chitosan used (cf. Table 1). In order to improve the WBC of the oven-dried CMCS, the foaming technique was applied in this study. Sodium bicarbonate, which is the most common blowing agent, did not perform well (data not shown), since the pH of the CMCS solution was higher than the pH that is necessary to start foaming (slightly acidic). Testing of acetone as a blowing agent also failed due to precipitation of CMCS by acetone (data not shown). *n*-Pentane had the best performance as the blowing agent for CMCS, since it was insoluble in water and had no effect on solubility of CMCS. The foaming with *n*-pentane depended only on the temperature and, due to its low boiling point (36 °C), raising the temperature to close to 60 °C accelerated the foam formation during the crosslinking reaction. Consequently, gas bubbles were captured inside the crosslinked network and resulted in stable foam and prevented shrinkage of the product during the oven-drying. Therefore, using this blowing agent resulted in SAPs with a porous structure and high WBC.

3.3. Optimization of the operating condition in the foaming technique

Response surface design is a statistical technique which is used to evaluate the effect of a number of variables on one or more measured responses. This technique reduces the numbers of the experiments compared to e.g. factorial design, while studying the effects of several factors (Qunyi & Ganwei, 2005). In this work the response surface design was applied to study the effect of amount of blowing and crosslinking agents and also the concentration of CMCS with different Mw on the WBC of the foam-dried SAPs.

For the CMCS with high Mw, the experiments were carried out in the range of 0.012–0.028 (g/g) glutaraldehyde, 0.3–0.7 (ml/ml) *n*-pentane and 1.5–2.5% of CMCS concentration. The contour surface plots of different WBCs with varying amounts of glutaraldehyde and *n*-pentane and concentrations show that the optimal condition to get the highest WBC is placed at the center point (Fig. 3). At this point, the average amount of WBC at 1 and 60 min in pure water is 55 and 85 (g/g), respectively. While the average of WBC in salt solution (after 1 min) and under centrifugal load (after 60 min) is 32 and 66 (g/g), respectively (Table 2). The same range of the variables was chosen for CMCS with medium Mw and the results are shown in Table 3. The contour plots in Fig. 4 show that the maximum amount of WBCs is obtained at the same center point as the one for high Mw CMCS. The average values for absorbency in water (1 min), water (60 min), salt (1 min) and CRC (60 min) were 52, 91, 33 and 66 (g/g), respectively (Table 3).

CMCS with low Mw showed different characteristics when subjected to the foaming technique, compared to medium and high Mw CMCSs. The optimal results were obtained at a center point of 0.04 (g/g) glutaraldehyde, 0.5 (g/g) *n*-pentane and 2% concentration of CMCS. The amount of glutaraldehyde and also the concentration at the optimum point is higher for the low molecular weight CMCS compared with the two others (Figs. 3–5). The maximum absorbency of this CMCS was 30, 64, 23 and 45 (g/g) for water (1 min), water (60 min), salt (1 min) and CRC (60 min), respectively (Table 4), which is lower than the ones for medium and high Mw CMCSs.

The coefficients of the second-order model for WBCs of high, medium and low molecular weight CMCS which were statistically significant and also the corresponding R^2 values are presented in Table 5. This table shows that the WBCs of medium Mw CMCS mainly depend on the amount of *n*-pentane, while the three investigated factors have no interactional effects on WBC at any investigated conditions. However, the linear and quadratic terms of concentration of the low Mw CMCS and also its interaction with the amount of glutaraldehyde are probably the most important factors for this CMCS. The average of R^2 values for WBCs of different SAPs is 78% (Table 5). This indicates that more than 78% of the total variations are explained by the models developed for the corresponding WBCs of different SAP prepared in this study.

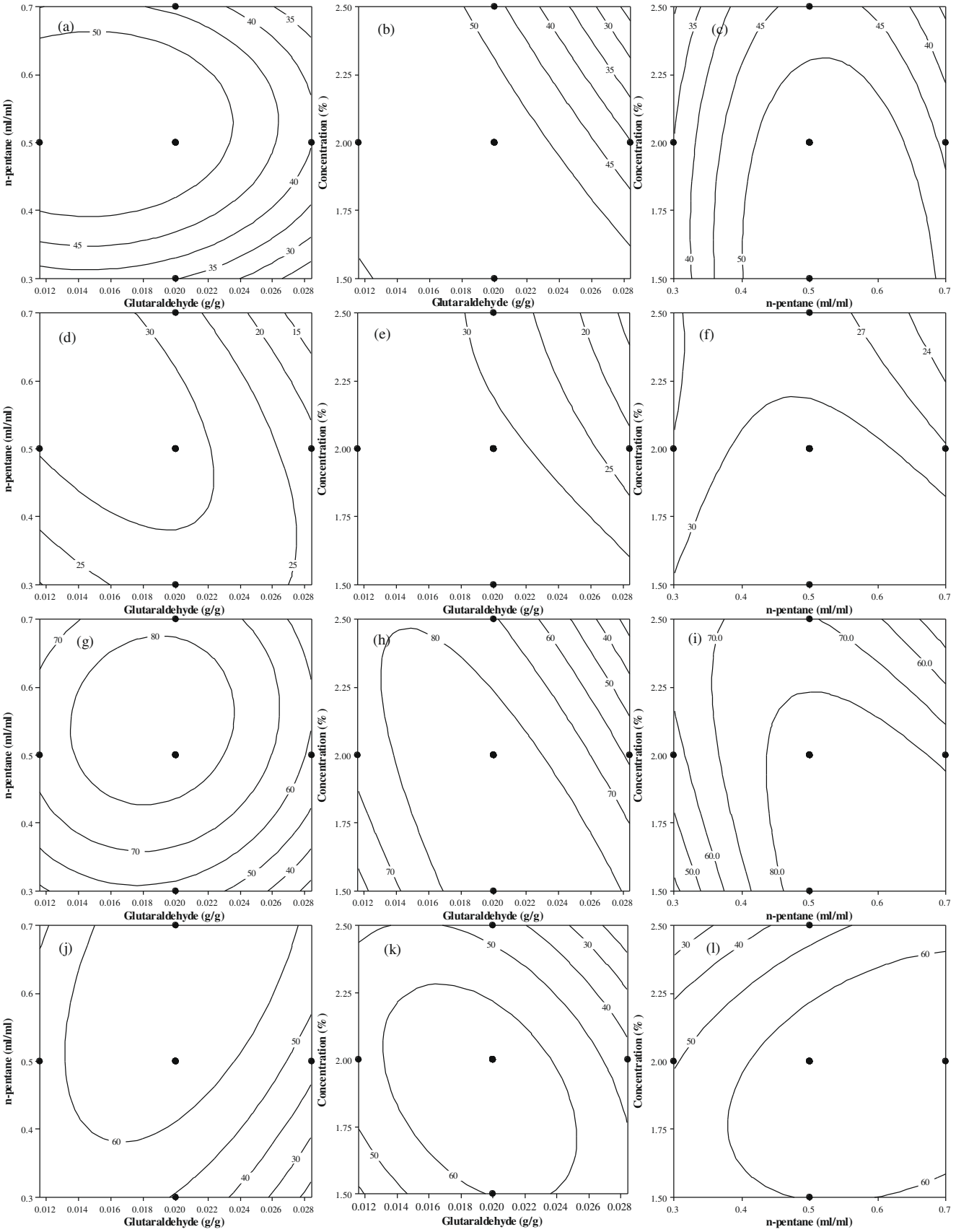

Fig. 3. The effect of concentration of high Mw CMCS and the amount of *n*-pentane and glutaraldehyde in the foaming technique on WBCs. The graphs show absorbency of (a–c) pure water after 1 min exposure, (d–f) salt water after 1 min exposure, (g–i) pure water after 60 min exposure, and (j–l) CRC after 60 min exposure.

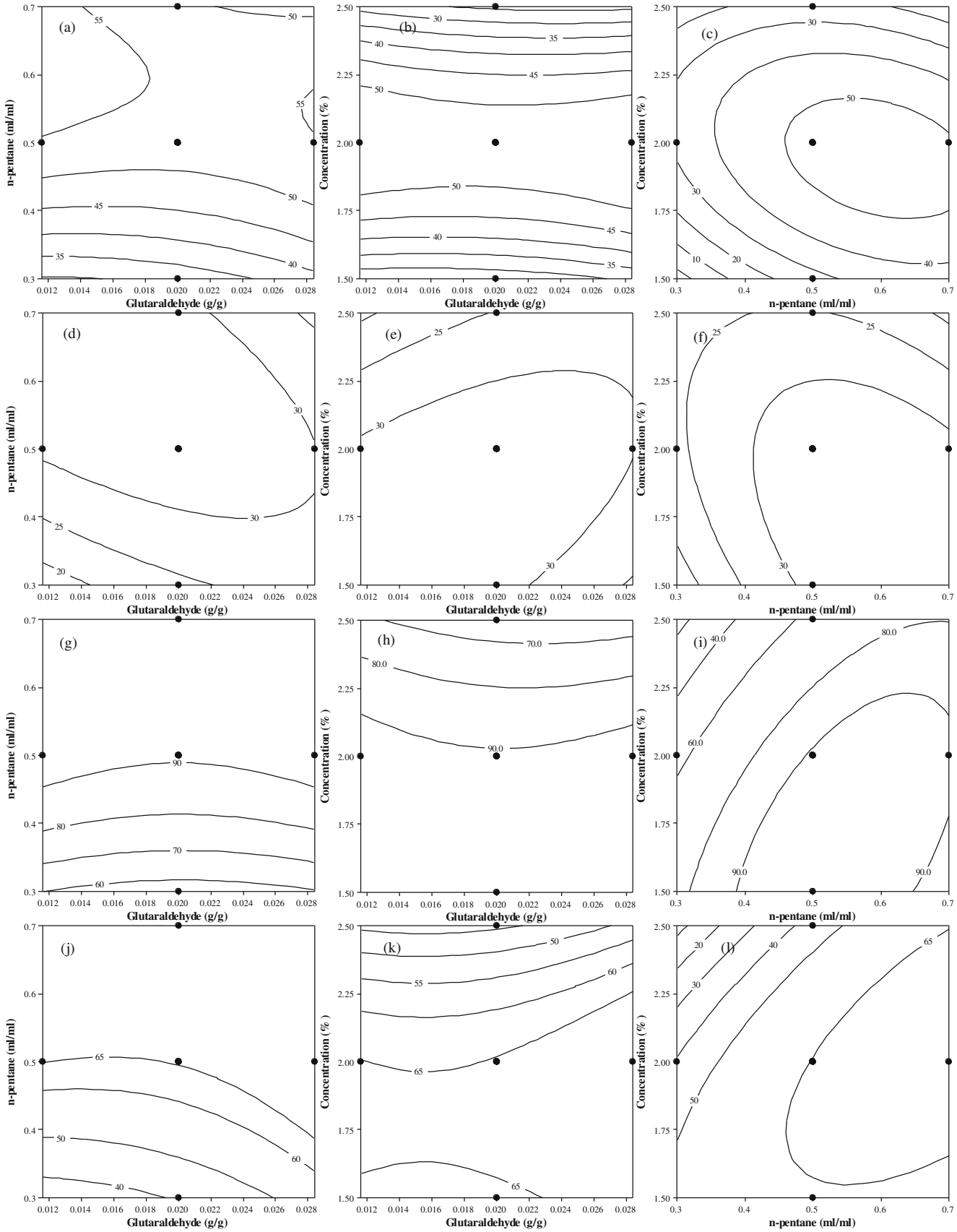

Fig. 4. The effect of concentration of medium Mw CMCS and the amount of *n*-pentane and glutaraldehyde in the foaming technique on WBCs. The graphs show absorbency of (a–c) pure water after 1 min exposure, (d–f) salt water after 1 min exposure, (g–i) pure water after 60 min exposure, and (j–l) CRC after 60 min exposure.

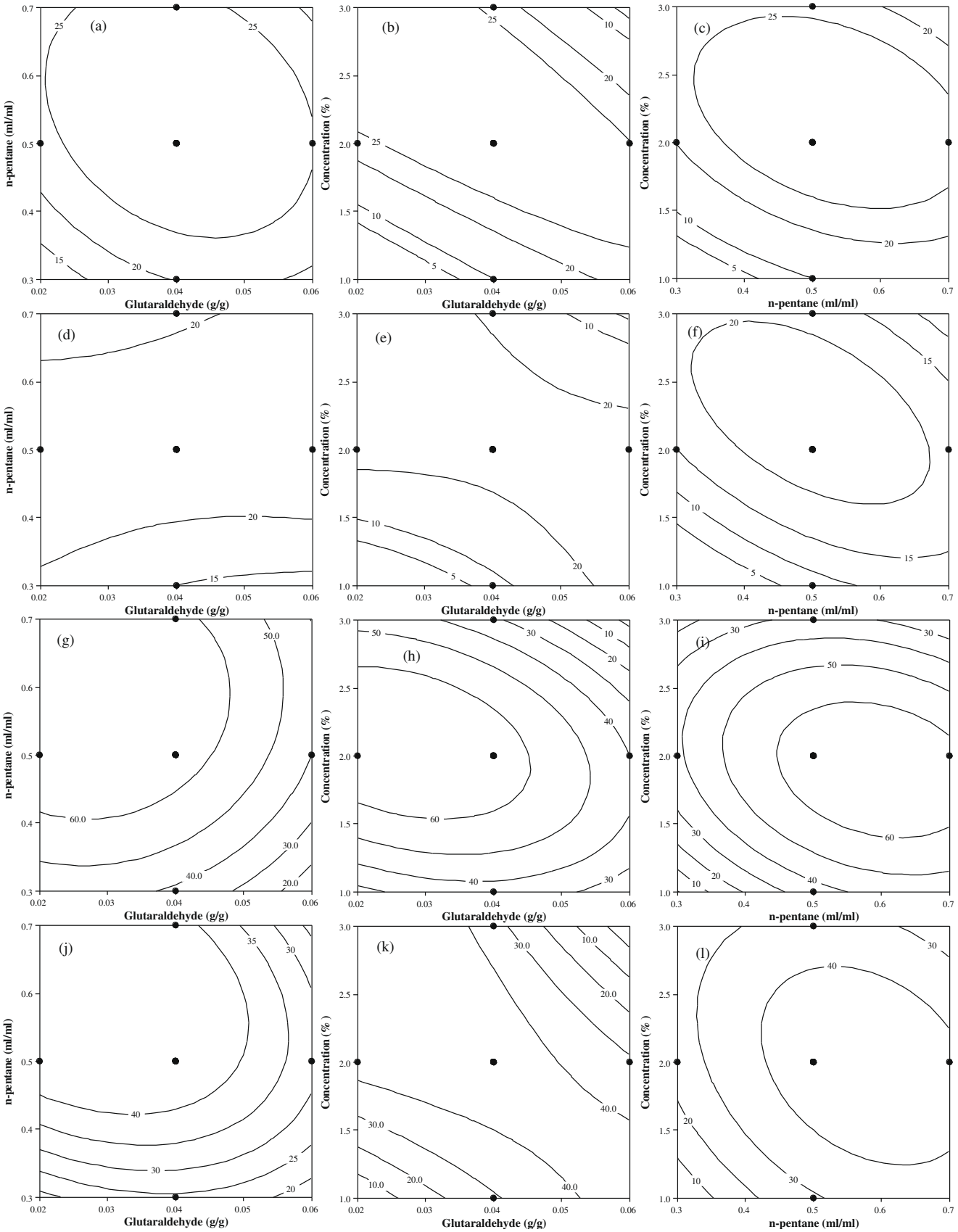

Fig. 5. The effect of concentration of low Mw CMCS and the amount of *n*-pentane and glutaraldehyde in the foaming technique on WBCs. The graphs show absorbency of (a–c) pure water after 1 min exposure, (d–f) salt water after 1 min exposure, (g–i) pure water after 60 min exposure, and (j–l) CRC after 60 min exposure.

Table 5
The estimated significant model coefficients* for WBCs of high, medium and low Mw foam-dried CMCS for uncoded variables presented in Tables 2–4.

CMCS	Absorbency	b_1	b_2	b_3	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}	b_0	R^2(%)
High	Water after 1 min	−7.7				−14.6					54.1	75
High	Salt solution[1] after 1 min	−4.4		−4.6	−5.6			−6.3			31.5	84
High	Water after 60 min	−7.6	10.1	−8.1	−19.4	−18.5			−18.5	−20.7	85.1	92
High	CRC[2] after 60 min		9.6	−7.4	−15.9						65.6	75
Med	Water after 1 min		9.6			−11.0	−27.2				52.5	90
Med	Salt solution[1] after 1 min		3.7			−5.0					32.6	74
Med	Water after 60 min		17.8	−16.4							91.0	79
Med	CRC[2] after 60 min		16.0	−9.5							65.4	77
Low	Water after 1 min			6.8			−13.2		−16.6		29.8	82
Low	Salt solution[1] after 1 min			5.3			9.9		−15.6		22.6	76
Low	Water after 60 min										64.3	57
Low	CRC[2] after 60 min		9.1						28.3		44.6	76

* Absorbency = $b_0 + b_1g + b_2p + b_3c + b_{11}g^2 + b_{22}p^2 + b_{33}c^2 + b_{12}gp + b_{13}gc + b_{23}pc + e$.
[1] 0.9% sodium chloride solution.
[2] Centrifuge Retention Capacity in water.

3.4. WBC of reference SAP

In this work the WBCs of reference SAPs were measured under identical conditions and the results are shown in Table 1. The L520 and 5A70 were able to absorb 285.1 and 597.2 (g/g), respectively, of pure water after 1 h. L520 showed better CRC and was able to retain 84.6% of absorbed water under the force; however, the WBC of 5A70 was 2.5 times more than the WBC of L520 in shorter time (1 min). Both L520 and 5A70 showed poor water absorbency in the presence of salt and they were only able to absorb 36.4% and 18.0%, respectively, of their capacity in 0.9% NaCl solution after 1 min (Table 1).

4. Discussion

Superabsorbents (SAP) used in the hygienic industry are crosslinked polymers of polyacrylates that are able to absorb huge amounts of water in short times (Buchholz & Graham, 1998). Porosity of the polymer network has important effects on the water-binding rate. Super-porous superabsorbents can be obtained by foaming techniques during the drying process (Kabiri et al., 2003a; Kabiri et al., 2003b; Omidian et al., 2005; Phan, 1994). In this work, a new foaming technique has been developed for production of SAPs from carboxymethyl chitosan. The obtained SAPs had elevated WBC in salt solution compared to reference synthetic SAPs. Two drying methods, freeze-drying and oven-drying, were used as a reference for evaluation of the new method.

Our results showed that by applying the freeze-drying method, absorbent materials with a high water-binding rate are obtained. The amount of absorbed water after 1 min by freeze-dried CMCS was comparable to commercial SAP and, unlike polyacrylates, their absorbency in the presence of salt did not decrease significantly (Table 1). By having those properties together with biodegradability and good absorbency in slightly acidic pHs (Chen et al., 2004), CMCS can be considered as a good source for production of SAP. In the freeze-drying technique, the position of crosslinked polymer chains remains unchanged. It results in easier diffusion of water into the SAP and increases the water-binding properties. In contrast, during oven-drying a shrinkage in the volume of samples occurs which leads to a significant decrease in the performance of the SAP. However, freeze-drying is an expensive method and from the industrial point of view, cheaper drying methods may be more applicable.

Two main reactions including crosslinking polymerization and foaming are involved in the production of modern commercial SAPs. The first reaction, called gelation, is harmonized with the second reaction–i.e. foaming to reach a homogeneous structure (Omidian et al., 2005). The same phenomenon was observed for CMCS in this work. The improvement of water-binding due to the foaming process was closely related to the progress of the gelation reaction. For the medium and high Mw CMCSs at all of the concentrations used in this study, gelation occurred after addition of glutaraldehyde, while for the low Mw CMCS no gelation was observed at the same conditions (i.e. the same concentration and the same amount of glutaraldehyde). The gelatinous hydrogel captured the blowing agent inside the polymer matrix and increased the stability of the prepared foam. This stable foam prevented the shrinkage of the samples during the oven-drying and increased the water absorbency. However, for the low molecular weight chitosan which did not form a strong gel, phase separation between the polymer solution and *n*-pentane resulted in fast evaporation of the blowing agent and a lower WBC compared to high and medium Mw. Increasing the concentration and the amount of glutaraldehyde accelerated the gelation process and improved the WBC of CMCS. Still, this improvement was limited due to formation of a rigid gel with a poor WBC at very high concentrations and very high amounts of glutaraldehyde.

5. Conclusion

SAP with high WBC and WBR has been produced from CMCS. Freeze-drying and foaming technique by using *n*-pentane as the blowing agent resulted in a porous structure of crosslinked carboxymethyl chitosan with good water-binding properties in both water and salt solutions.

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