A new approach to increasing the equilibrium swelling ratio of the composite superabsorbents based on carboxymethyl cellulose sodium salt

Andrey Sorokin · Pavel Sukhanov · Vasiliy Popov · Sergey Kannykin · Maria Lavlinskaya

Abstract The work aims to research the effect of dibutyl succinate on the water-absorbing and water-holding properties of the composite superabsorbents enriched in the sodium salt of carboxymethyl cellulose. The synthesized composite superabsorbents with a different content of dibutyl succinate were analyzed by FTIR, SEM, XRD, DSC, and rheological measurements; equilibrium swelling ratio values, Q_e, in distilled water and in a saline solution were determined; and swelling kinetics, water-holding properties, and regeneration ability were researched. It was found that adding 5% w of dibutyl succinate increases Q_e values in distilled water up to 51% compared to blank superabsorbents. The effect of a plasticizer is due to its selective interaction with intramolecular H-bond-forming links, which increases the flexibility of the polymeric network and the availability of sorption sites for water molecules. The non-outwashing of a plasticizer in an aqueous medium was confirmed by HPLC–MS. The presence of dibutyl succinate does not change the water absorption mechanism controlled by chemisorption and pseudo-Fickian diffusion of water molecules but accelerates the equilibrium swelling ratio achievement. Also, there is no significant impact of a plasticizer on the water-holding properties of the synthesized superabsorbents at 80 °C, as well as on their reusability, which retains during several swelling-deswelling cycles. So, dibutyl succinate may be applied as an efficient plasticizer enhancing water sorption properties of the composite superabsorbents based on carboxymethyl cellulose sodium salt.

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Graphical abstract
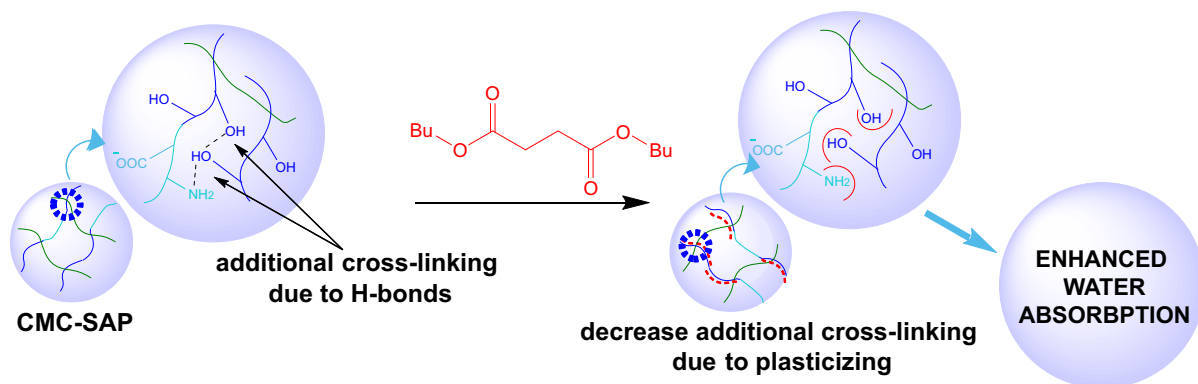
Keywords Composite superabsorbents · Plasticization · Dibutyl succinate · Water sorption properties · Swelling ratio

Introduction

Currently, much attention of researchers around the world is attracted to the development of superabsorbents (SAPs) which are cross-linked polymeric hydrogel materials capable of absorbing and retaining significant amounts of water, hundreds and thousands of times higher than their weight (Mignon et al. 2019). Such polymers are used in various fields of human activity, but they are especially widely used in biomedicine (Samadian et al. 2020; Amiri et al. 2021), for the controlled release of some drugs such as diclofenac sodium (Hosseinzadeh 2010; Pourjavadi et al. 2013; Haseeb et al. 2016), tetracycline (Jeong et al. 2018), doxorubicin (Khan et al. 2019), diethyl carbamazine citrate (Mehta et al. 2021), etc.; as well as in the creation of personal hygiene products (Lacoste et al. 2019) and agriculture (Li and Chen 2019; Saha et al. 2020).

Earlier research describing the creation of SAPs, also as known as hydrogels, dealt with the synthesis of cross-linked polymers based on acrylic acid derivatives (Mignon et al. 2019). However, it became clear that the use of such polymers on a commercial scale would have a negative impact on the environment. This brought about the development of eco-friendly biodegradable polymers also retaining a high water absorption

capacity (Qureshi et al. 2020). Most of these studies are devoted to the incorporation of polysaccharides into polyacrylic matrices, or the creation of SAPs based on modified polysaccharides and their interpolyelectrolyte complexes (Lacoste et al. 2019; Mignon et al. 2019; Ravishankar and Dhamodharan 2020). However, fully polysaccharide SAPs, also known as natural or bioSAPs, are often inferior in water absorption capacity to synthetic polyacrylate ones (Lv et al. 2018; Ravishankar and Dhamodharan 2020). At the same time, the swelling ratio of composites containing both natural and synthetic moieties significantly depends on the content and type of polysaccharides and decreases sharply with the growth of their content (Sorokin and Lavlinskaya 2021).

The main factor determining the ability of the SAP network to swell is the crosslinking degree (Chavda and Patel 2011; Khan and Ranjha 2014; Qureshi et al. 2020). The higher it is, the more rigid the polymer structure, and the more difficult it is for water molecules to penetrate and interact with sorption centers. All this reduces the ability of the SAPs to absorb water. Therefore, in most investigations connected to the creation of composite SAPs, the best results on the swelling ratio were obtained while using a small amount of a crosslinker (less than 1% w) in the polymerization mixture. However, the viscosity of the reaction mass enriched in polysaccharides is quite high; 3D polymeric network formation is complicated with a low content of a crosslinker; and the number of side processes leading to the formation of undesirable products increases (Suo et al. 2006).

One of the possible ways to solve the problem of increasing the water absorption capacity of composite SAPs enriched in polysaccharides is the introduction of plasticizers into the polymer structure. Such additives enhance the segmental mobility of the polymeric networks (Vieira et al. 2011; Wypych 2017), which should improve the availability of sorption centers for interaction with water molecules and increase the swelling degree of the resulting composites.

Unfortunately, at the moment there is no single theory describing the mechanism of interaction of the polymers with the plasticizers (Wypych 2017); therefore, these components are selected empirically for each polymer. According to the literature data (Lin et al. 2000; Vieira et al. 2011; Wypych 2017), the plasticizers most commonly used for polyacrylates are polyols and their ethers and esters with fat and (di)carboxylic acids, including toxic diphtatalates, (di)benzoates, as well as amines and amides. For the commonly used polysaccharides, such as cellulose and its derivatives, the common plasticizers are citrates and dicarboxylic acid esters. It can be assumed that the dicarboxylic acid esters are most suitable as plasticizers for the polyacrylate-cellulose derivatives composite.

In connection with the foregoing, the current work aims to research the effect of dibutyl succinate (DiBuSuc) on the water-absorbing and water-holding properties of the composite superabsorbents enriched in the sodium salt of carboxymethyl cellulose.

Materials and methods

Materials

Carboxymethyl cellulose sodium salt (CMC) (food grade, > 99%), with an average M_w 10 000, degree of substitution 0.72, the viscosity of 1% water solution at 25 °C 11,448 mPa × s, was purchased from Stoing, Russia, and used for the SAP synthesis without any purification. Acrylamide (AAm) (extra pure, > 98%), acrylic acid (AA) (extra pure, > 98%), *N,N*-methylene-*bis*-acrylamide (MBAAm) (> 98%), potassium persulfate (PPS) (> 98%), and potassium hydroxide (> 98%), all Acros Organic, USA, were applied in SAP synthesis. AA with T_b = 45 °C/ 15 Hgmm was previously distilled in a vacuum, AAm and MBAAm were recrystallized in ethyl acetate, and PPS was recrystallized in deionized water before the work.

Succinic acid (> 98%), butanol-1(anhydrous 99.5%), and *p*-toulenesulfonic acid (> 98%), all Acros Organic, USA, were used for dibutyl succinate synthesis. Distilled water (21 MΩ, pH = 6.7 ± 0.2), ethanol (anhydrous 99.5%, ReaKhim, Russia), and ethyl acetate (chromatography grade, > 99%, ReaKhim, Russia) were used as solvents without any treatments.

Dibutyl succinate synthesis

Dibutyl succinate was used as a plasticizer in the work. To obtain it, 11.8 g (0.1 mol) of succinic acid, 23 ml (0.25 mol) of butanol-1 and, 1 g (0.006 mol) of *p*-toluenesulfonic acid as a catalyzer were placed in a one-necked round-bottom flask equipped with a Dean-Stark trap containing toluene, a condenser, and a magnetic stirrer. The mixture was vigorously stirred until full acid dissolution, and refluxed for 6 h. The resulting product was purified by vacuum distillation at 97 °C/ 10 Hgmm. HPLC–MS testing of the synthesized dibutyl succinate showed a fineness of more than 99%. The yield of the product was 78%.

Superabsorbent synthesis

For CMC-SAP synthesis, several amounts of CMC (Table 1) were placed in a thermostatically controlled reactor equipped with a condenser, a mechanical stirrer, and a nitrogen line for degassing of the reaction mixture, and dissolved under vigorous stirring in 50 mL of distilled water. Then, 10 mL of a water solution containing AAm, AA, MBAAm, and PPS (Table 1) was added to the reactor and kept at 80 °C for 2 h. The product obtained was ground with 1.63 g of KOH in 10 mL of deionized water, immersed in ethanol overnight to remove soluble compounds, milled with 2, 5, or 10% w dibutyl succinate in 5 mL of ethanol, and dried in a vacuum to a constant weight. After drying, the yield of the products was 89–95%. The resulting CMC-SAPs are insoluble in water, ethanol, propanol-2, and acetone.

Instrumental characterization

FTIR

For CMC-SAP structure characterization, FTIR ATR was used. The spectra were obtained by using a Bruker

Table 1 CMC-SAP synthesis conditions

No	Sample name	CMC, g	AA, g	AAm, g	MBAAm, g	PPS, g	DiBu-Suc, g	Yield, %
1	CMC-SAP-10–0	0.440	3.000	1.000	0.022	0.044	0	91
2	CMC-SAP-10–2	0.440	3.000	1.000	0.022	0.044	0.088	93
3	CMC-SAP-10–5	0.440	3.000	1.000	0.022	0.044	0.220	89
4	CMC-SAP-10–10	0.440	3.000	1.000	0.022	0.044	0.440	94
5	CMC-SAP-20–0	1.000	3.000	1.000	0.025	0.050	0	92
6	CMC-SAP-20–2	1.000	3.000	1.000	0.025	0.050	0.100	95
7	CMC-SAP-20–5	1.000	3.000	1.000	0.025	0.050	0.250	90
8	CMC-SAP-20–10	1.000	3.000	1.000	0.025	0.050	0.500	92

Vertex 70 instrument (Bruker Optics, Germany) with Fourier transducer in the 400–4000 cm^{-1} frequency range, 32 scannings during 1 cycle; the number of cycles was 4. The samples were in powder form.

SEM

For CMC-SAP surface research, the SEM method was applied. The SEM images were obtained using the scanning microscope JEOL JSM-6380LV (JEOL, Japan). The samples analyzed were sprayed with gold before conducting the scanning. The thickness of the gold film was 10 nm.

DSC

For glass transition temperature (T_g) determination, the DSC method was utilized. The research was performed on STA 449 F3 Jupiter simultaneous thermal analyzer (Netzsch, Germany) in a capped aluminum pan in a He atmosphere with a heat rate of 10 °C/min from 20 °C to 200 °C. The relaxation transition of the glass transition is accompanied by an abrupt growth in the heat capacity of the polymer and is fixed on the DSC curve as an inflexion. To obtain accurate results for this parameter on the DSC curve, it is necessary to select the point corresponding to the middle fold lines.

XRD

To investigate the influence of dibutyl succinate on the crystallinity of CMC-SAPs, the XRD method was used. The study was conducted with an Empyrean B.V. diffractometer (PANalytical B.V., Netherlands) equipped with a Cu-K_α radiation source (λ = 1.54 nm, 45 kV and 35 mA) in scattering angle range 2θ from 5° to 60° with a resolution of 0.1°, at a scanning speed of 0.2°/min.

Rheological research

To study the rheological properties and mechanical strength of the swollen particles of the synthesized CMC-SAPs, the rheological method was used. A stress-controlled Gemini HRnano rheometer (Malvern Instruments, UK) equipped with a solvent-trap and moisture controlling systems was applied for rheological measurements. The operating temperature was 210 °C controlled by a Peltier plate. The experiments were performed using acrylic parallel plate geometry (40 mm diameter, 1 mm gap). Three repetitions of measurements were carried out for each sample.

HPLC–MS

To confirm the obtaining of DiBu-Suc and its fineness, as well as outwashing of the plasticizer in aqueous media, the HPLC–MS method was applied. Agilent 1269 Infinity instrument equipped with an Agilent 6230 TOF LC/MS detector (Agilent Technologies, USA) and Poroshell 120 EC-C18 column (4.6 × 50 mm, 2.7 μm) was used for the investigation. The ionization method was double electrospray; registration was carried out in positive polarity; the registered mass range was 50–2000. Acetonitrile was utilized as eluent with a flow rate of 0.4 mL/min.

Swelling research

The equilibrium swelling ratio/swelling kinetics research in distilled water or 0.15 M NaCl aqueous solution was performed as described by Sorokin and Lavlinskaya 2021. The equilibrium swelling ratio, Q_e, or swelling ratio at time t, Q_t, is expressed as follows:

$$Q = \frac{m_1 - m_0}{m_0} \tag{1}$$

where m_1 and m_0 are the weights of swollen and dry CMC-SAP samples, respectively. The number of samples used for every synthesized SAP in the swelling ratio investigation was 3 ($n = 3$, $P = 0.95$). The results obtained were analyzed using MS Excel software and expressed as means ± SD from three independent experiments.

To study the water absorption mechanism and the effect of a plasticizer on it, swelling kinetics data were processed by common mathematical kinetic swelling models. The pseudo-first-order swelling kinetic model is expressed as (Lagergren 1898):

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t, \tag{2}$$

the pseudo-second-order swelling kinetic model is described by the following equations (Ho and McKay 1999):

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}, \tag{3}$$

and Ritger-Peppas model is characterized as (Peppas and Khare 1993):

$$F = \frac{Q_t}{Q_e} = k \times t^n, \tag{4}$$

taking the logarithm expression 4:

$$\ln F = \ln Q_t - \ln Q_e = \ln k + n \ln t, \tag{5}$$

where Q_e (g/g) and Q_t (g/g) are the swelling ratios at equilibrium and time t, respectively; k_2 (g•mg^{-1}min^{-1}) is the rate constant of the pseudo-second-order model; F is the fractional swelling rate at time t; k is the structural parameter, and n is the swelling exponent which exhibits the type of diffusion. The Chi-square (χ^2) non-parametric test with a significance level of 0.05 and a degree of freedom = 9, $\chi_c^2 = 15.5$ was used to confirm the results.

Investigating water retention and regeneration

Water retention investigation and the regeneration study are performed as described by Sorokin and Lavlinskaya 2021. The water retention, R, was expressed as follows:

$$R = \frac{m_1}{m_0} \times 100, \tag{6}$$

where m_0 and m_1 are the weight of the swollen CMC-SAP sample and the weight of the CMC-SAP sample after a partial water loss in each time interval, respectively.

Results and discussions

Synthesis and characterization of CMC-SAPs

The composite superabsorbents CMC-SAP were prepared in an aqueous solution at 80 °C with the use of a carboxymethyl cellulose sodium salt (CMC) as a source of the biodegradable links. The ratio of comonomers, cross-linker, initiator, as well as a concentration of the polymerization feed, was chosen based on our earlier research (Sorokin and Lavlinskaya 2021). The synthesis of the CMC-SAPs was performed in conditions providing the highest values of the equilibrium swelling ratio. The polymerization mixtures contain 10 or 20% w of CMC, denoted as CMC-SAP-10 and CMC-SAP-20, respectively. A further increase in the polysaccharide concentration led to a significant increase in the viscosity of the reaction feed and the failure to polymerize.

The possible reaction mechanism (Liu et al. 2019) includes potassium persulfate (PPS) initiator termodecay following the production of sulfate ion-radicals interacting with OH-groups of CMC, resulting in reactive radicals on polyglycoside backbones (Fig. 1). Next, comonomers–acrylic acid (AA), acrylamide (AAm), and N,N-methylene-bis-acrylamide (MBAAm)–react with CMC backbone radicals in a random order, forming growing polymeric chains. Their termination occurs due to a recombination of the macrochains, providing a dimensional composite network.

The formation of the CMC-SAPs was confirmed by FTIR (Fig. 2). The spectra of CMC-SAPs contain some characteristic bands near the following

Fig. 1 Possible mechanism
of the CMC-SAP formation
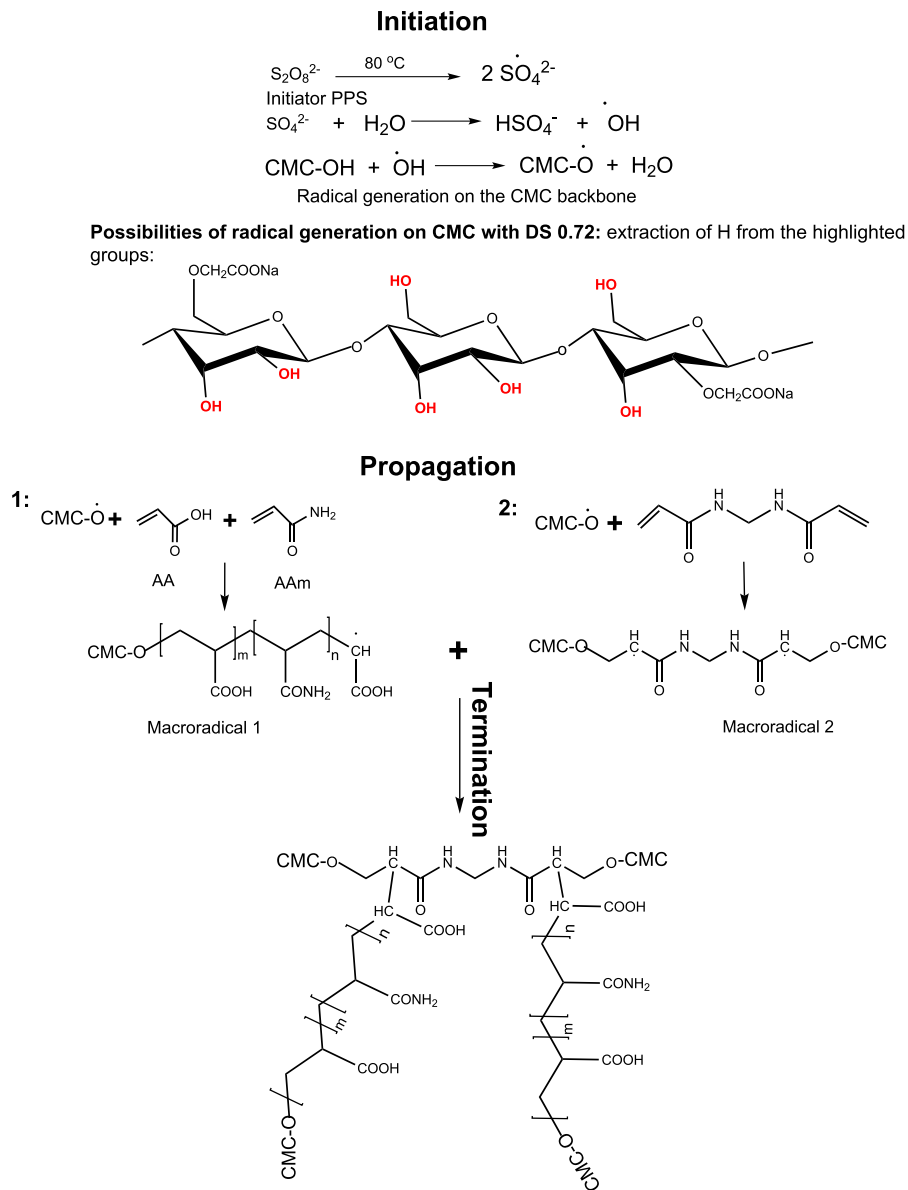
wavenumber: 1020 cm^{-1}, 1052 cm^{-1}, and 1120 cm^{-1} attributed to vibrations of the skeleton and ester bond C–O–C of the pyranose cycles, respectively (Reshma et al. 2020); 1399 cm^{-1} and 1448 cm^{-1} representing vibrations of (non)dissociated carboxylic groups (Bao et al. 2011); 1556 cm^{-1} and 1662 cm^{-1} ascribed to the stretching vibrations of the NH$_2$-groups and C=O, respectively (Jeong et al. 2020); 2852 cm^{-1} characterizing secondary amino-group vibrations; 2935 cm^{-1} related to vibrations of the C-H bonds, and a broad band at 3200–3400 cm^{-1}

due to the vibrations of the associated water molecules (Wang et al. 2017).

The surface of the CMC-SAPs obtained was characterized by SEM. Figure 3 represents the SEM images of the surfaces of the synthesized CMC-SAPs. As can be seen, with the increase in the CMC content in the superabsorbent polymerization feeds, the surface of the resulting SAPs is becoming more porous and developed. However, the equilibrium swelling ratio of the products obtained is decreased with CMC content growth, both in distilled water and
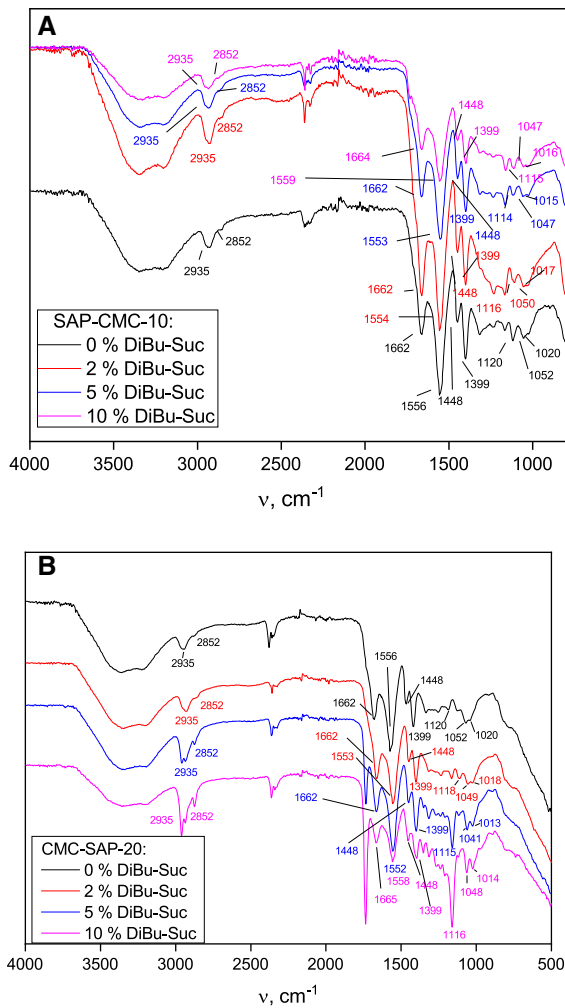
Fig. 2 FTIR spectra of CMC-SAPs: **a** CMC-SAP-10; **b** CMC-SAP-20

Fig. 3 SEM images of the CMC-SAPs: **a** CMC-SAP-10; **b** CMC-SAP-20

saline solution (Table 2). This is because acrylic polymers have a higher water affinity compared to CMC (Dai et al. 2019).

The influence of the plasticizer on CMC-SAP water-absorbing and water-holding properties

The SAP ability to absorb and retain a huge amount of water is caused by the hydrogen bond formations between water molecules and SAP sorption sites (Ganji et al. 2010; Mignon et al. 2019). The more sorption sites are sterically available, the more water SAPs can absorb. To improve the availability of the sorption sites, the flexibility and mobility of the polymeric network moieties need to be enhanced.
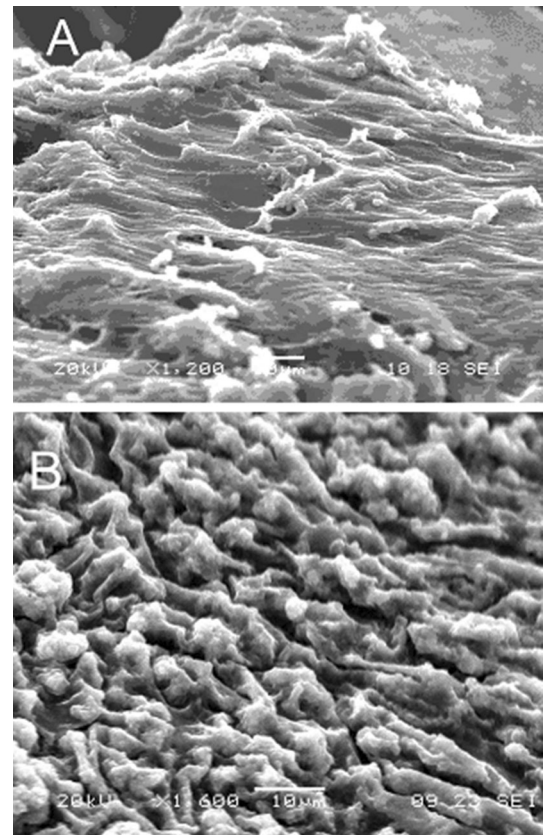
Most of the research dealing with SAP development is done by varying of comonomer ratio or cross-linker amount (Suo et al. 2006; Singh et al. 2018; Fang et al. 2018; Behrouzi et al. 2018; Fang et al. 2019; Khusbu et al. 2019; Chen et al. 2021). Polymer plasticization is a common way to tune the polymer properties related to the flexibility of the macromolecular chains or networks. Lin et al. (2000) show that plasticizer use can increase the swelling ratio and reduce glass transition temperature of *Eudragit* acrylic resins, confirming the enhancement of polymeric network flexibility. Additionally, a review by Vieira et al. (2011) describes plasticization additives for natural polymer films also modifying polymeric flexibility. However, the influence of plasticizers on SAP water-absorbing and water-holding properties has not been researched yet. In this work, dibutyl succinate (DiBu-Suc) was used as a plasticizer for composite SAPs based on carboxymethyl cellulose sodium salt.

Table 2 Equilibrium swelling ratio, Q_e, for synthesized CMC-SAPs

DiBu-Suc content, % w	Q_e			
	Distilled water		0.15 M NaCl aqueous solution	
	CMC-SAP-10	CMC-SAP-20	CMC-SAP-10	CMC-SAP-20
0	1061 ± 51	398 ± 19	81 ± 2	75 ± 2
2	981 ± 44	341 ± 16	85 ± 2	78 ± 2
5	1289 ± 59	603 ± 28	90 ± 3	81 ± 3
10	699 ± 33	302 ± 14	86 ± 3	79 ± 2

Equilibrium swelling ratio, Q_e, is one of the most important characteristics of SAPs, determining the efficiency of their use. Table 2 describes Q_e data in distilled water and a saline solution.

As can be seen from the data obtained, the presence of varying amounts of DiBu-Suc has a different effect on the equilibrium swelling ratio. The highest Q_e values are achieved for CMC-SAPs containing 5% w of plasticizer. The equilibrium swelling ratio is lower for the SAPs with 2% DiBu-Suc compared to the ones without an additive. The same is observed for samples containing 10% w of the plasticizer.

The main reason for the decrease in the SAP swelling ratio with a rise in the carbohydrate polymer content in the polymeric matrix is additional crosslinking of the three-dimensional network due to large intra- and intermolecular hydrogen bonds characterizing polysaccharide macromolecules. Therefore, when searching for a plasticizer for a composite SAP, it is necessary to select a compound that will act primarily on links prone to the formation of H-bonds. The results of studying the effect of dibutyl succinate on the equilibrium swelling ratio can be interpreted as follows: 2% w is an insufficient amount of additive to change the density of hydrogen bonds inside the polymeric network; so, the Q_e values obtained for a blank sample and SAPs with 2% w of the plasticizer are practically equal, taking into account the experimental error. Next, 5% w of DiBu-Suc is the optimal amount which increases the equilibrium swelling ratio by 21% for CMC-SAP-10 and by 51% for CMC-SAP-20. A rise in the amount of the plasticizer to 10% w leads to a reduction in the values of the equilibrium swelling ratio of CMC-SAP, which is due to the partial absorption of excessive amounts of the DiBu-Suc on the acrylate moieties. A more significant increase in a Q_e value for the CMC-SAP-20–5 sample confirms the

assumption about a selective effect of the plasticizer on intramolecular H-bond-forming links.

FTIR data also confirm the hypothesis about the selective effect of the plasticizer on the intramolecular H-bond-forming links (Table 3). In the FTIR spectra, a decrease in the wavenumbers is observed for the bands characterizing the vibrations of the pyranose rings and primary amino groups, which indicates a weakening of the interactions between them (Shatalov et al. 2016). However, with a growth in the content of dibutyl succinate to 10% w, an increase in the wavenumber is observed for the bands corresponding to the vibrations of the carbonyl groups of the acrylate segments of the superabsorbent matrix, which suggests interactions between them and the additive.

The assumption about the action of the plasticizer which hinders the formation of hydrogen bonds within the superabsorbent network is also confirmed by the data of X-ray diffraction (Fig. 4). To prevent the influence of water on the intensity and shape of the XRD signals (Hatakeyama et al. 2004; Fang and Catchmark 2014), SAP samples were carefully dried before the research. The XRD pattern of CMC contains the peak at $2\theta = 21°$ corresponding to the region of a higher crystallinity due to the intra- and intermolecular hydrogen bonds between hydroxyl groups of pyranose cycles (Salleh et al. 2019). The intensity of this peak decreases after CMC-SAP-20–0 formation because a part of CMC hydroxyl groups had been involved in polymerization. In the presence of a plasticizer, the intensity of a abovementioned peak, as well as total XRD signals, also decreases, confirming the reduction of the CMC-SAP-20–5 crystallinity.

Another parameter characterizing segment mobility and intersegmentation interactions is the glass transition temperature T_g. The higher the value of T_g, the stronger the aforementioned interaction, and, as a consequence, the availability of sorption centers is

Table 3 The FTIR and T_g characterization of CMC-SAPs depending on plasticizer content

Sample name	T_g, °C	ΔT_g, °C	Wavenumber, v, cm^{-1}	Δv, cm^{-1}	FTIR band description
CMC-SAP-10–0	185.9	–	1020	–	skeleton vibrations of pyranose cycles
			1052		skeleton vibrations of pyranose cycles
			1120		vibrations of C–O–C bond of pyranose cycles
			1556		NH$_2$ stretching vibrations
			1662		C=O stretching vibrations
CMC-SAP-10–2	185.3	− 0.6	1017	− 3	skeleton vibrations of pyranose cycles
			1050	− 2	skeleton vibrations of pyranose cycles
			1116	− 4	vibrations of C–O–C bond of pyranose cycles
			1554	− 2	NH$_2$ stretching vibrations
			1662	0	C=O stretching vibrations
CMC-SAP-10–5	184.2	− 1.7	1015	− 5	skeleton vibrations of pyranose cycles
			1047	− 5	skeleton vibrations of pyranose cycles
			1113	− 6	vibrations of C–O–C bond of pyranose cycles
			1553	− 3	NH$_2$ stretching vibrations
			1662	0	C=O stretching vibrations
CMC-SAP-10–10	187.5	+ 2.4	1016	− 4	skeleton vibrations of pyranose cycles
			1047	− 5	skeleton vibrations of pyranose cycles
			1115	− 5	vibrations of C–O–C bond of pyranose cycles
			1559	+ 3	NH$_2$ stretching vibrations
			1664	+ 2	C=O stretching vibrations
CMC-SAP-20–0	190.2	–	1020	–	skeleton vibrations of pyranose cycles
			1052		skeleton vibrations of pyranose cycles
			1120		vibrations of C–O–C bond of pyranose cycles
			1556		NH$_2$ stretching vibrations
			1662		C=O stretching vibrations
CMC-SAP-20–2	189.1	− 0.3	1018	− 2	skeleton vibrations of pyranose cycles
			1049	− 3	skeleton vibrations of pyranose cycles
			1118	− 2	vibrations of C–O–C bond of pyranose cycles
			1553	− 3	NH$_2$ stretching vibrations
			1662	0	C=O stretching vibrations
CMC-SAP-20–5	186.1	− 4.1	1013	− 7	skeleton vibrations of pyranose cycles
			1041	− 9	skeleton vibrations of pyranose cycles
			1115	− 5	vibrations of C–O–C bond of pyranose cycles
			1552	− 4	NH$_2$ stretching vibrations
			1662	0	C=O stretching vibrations
CMC-SAP-20–10	191.2	+ 0.9	1014	− 6	skeleton vibrations of pyranose cycles
			1048	− 4	skeleton vibrations of pyranose cycles
			1116	− 4	vibrations of C–O–C bond of pyranose cycles
			1558	+ 2	NH$_2$ stretching vibrations
			1665	+ 3	C=O stretching vibrations

difficult for a reaction with water molecules. Therefore, the presence of a plasticizer has to reduce T_g, confirming the decrease of H-bond formations and other interactions. The data of T_g values obtained by DSC are presented in Table 3. As can be seen from the data obtained (Fig. 5), the DSC curves are slightly
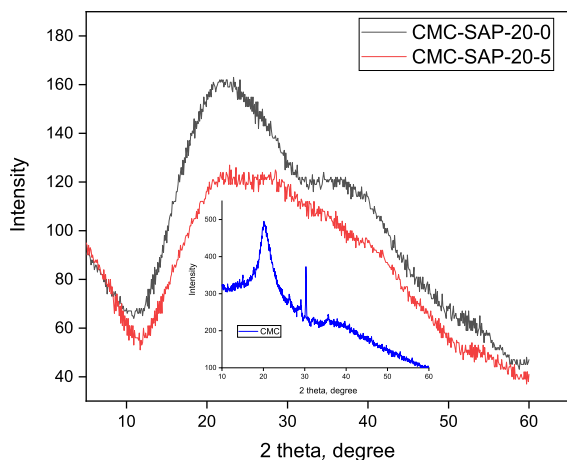
Fig. 4 XRD patterns of the CMC-SAPs

Fig. 5 DSC curves of the CMC-SAPs

changed and become sharper with the growth of dibutyl succinate content. Moreover, the glass transition temperature is reduced in the presence of 2–5% w of DiBu-Suc, and the minimal T_g values are achieved for SAPs containing 5% w of a plasticizer; then a slight rise in glass transition temperature is observed. The results of the DSC research confirm our hypothesis.

The presence of a plasticizer also affects the rheological properties of SAPs. These features of the synthesized CMC-SAPs were researched by the rheological method. The linear viscoelastic (LVE) regime was used for stress sweep tests. Storage modulus, G', and loss modulus, G'', are independent of the applied stress in this regime; however, the deviation of the value of both moduli from linearity is observed as the applied stress increases (Fig. 6a). The maximum stress up to which G' remains constant is called the critical stress, σ_c, characterizing a transition between linear and nonlinear regimes. The critical stress can be taken as the dynamic yield stress value. This means that below the critical stress the system behaves like an elastic solid. At the externally applied stress beyond σ_c, the internal network structure started to break down and the material subsequently flowed like a liquid (Seetapan et al. 2011). The data represented shows that CMC-SAP-20–0 has larger critical stress and a wider LVE region than those of CMC-SAP-20–5, indicating its better resistance to the external stresses.

Moreover, the value of tan δ, which is the ratio of G'' to G', was calculated to measure the strength of the interaction within the polymer system and represented as a function of stress (Fig. 6b). If the value of tan δ is
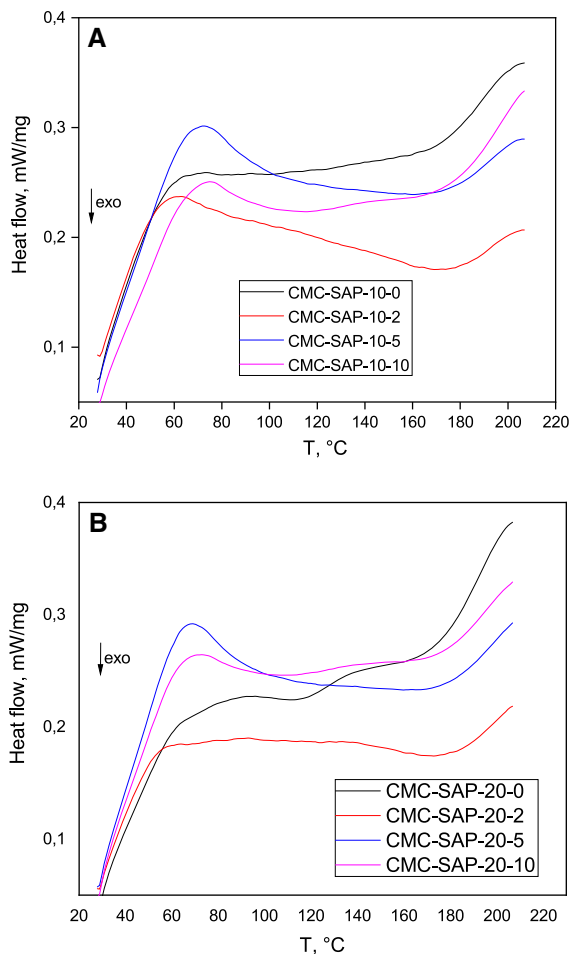
larger than 1 ($G'' > G'$), the system behaves like a liquid, whereas if the value of tan δ is smaller than 1 ($G'' < G'$), the system demonstrates solid-like (gel or network) behaviour. The results shown in this figure indicate that CMC-SAP-20–5, which has a higher water absorption capacity compared to CMC-SAP-20–0, possesses less gel strength due to its higher value of tan δ. Thus, it can be concluded that the gel strength is inversely related to its water absorption capacity, which is due to DiBu-Suc presence (Seetapan et al. 2011). The conducted rheological studies also confirm the effectiveness of the proposed plasticizer.

The swelling medium also affects the water-absorbing properties of the SAPs. The presence of electrolytes reduces the equilibrium swelling ratio due to the influence of osmotic pressure and the screening effect of metal ions (Mahon et al. 2020; Sorokin and
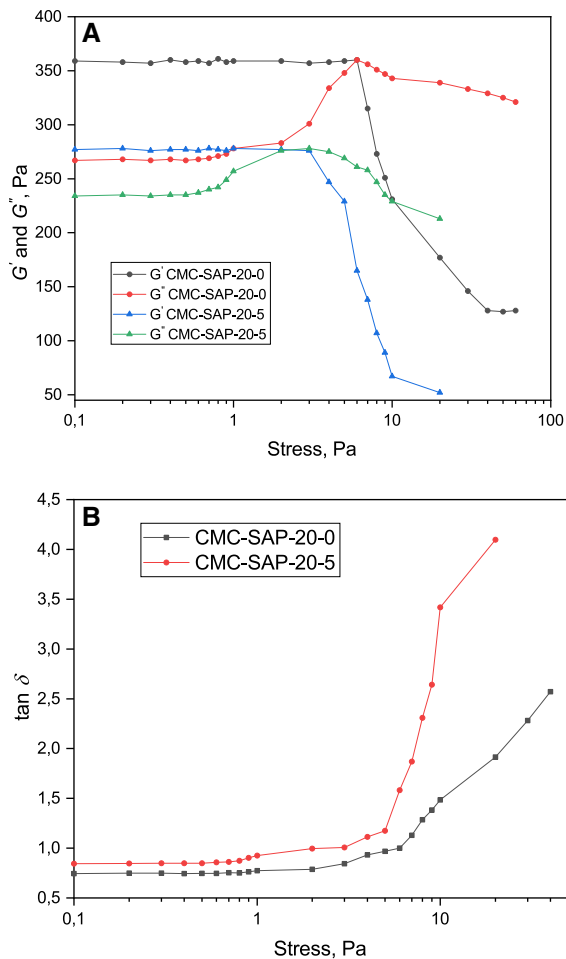
Fig. 6 Viscoelastic features of the CMC-SAPs in distilled water

Lavlinskaya 2021). The estimation of DiBu-Suc presence on the Q_e values in a saline solution shows that there is no significant effect on those values (Table 2.). The Q_e values decrease sharply in the 0.15 M NaCl aqueous solution compared to the ones in distilled water for all plasticizer contents.

Therefore, we found that dibutyl succinate enhances the equilibrium swelling ratio of composite SAPs based on carboxymethyl cellulose sodium salt due to the reduced intersegmental interaction of SAP matrixes. However, one of the most important requirements for plasticizers is non-outwashing from polymer. The water extract was analyzed by HPLC–MS after 24-h contact with CMC-SAPs. It was found that DiBu-Suc concentration in water for all samples is below the limit of detection.

An investigation of water absorption kinetics allows us to compare the rate of swelling for SAPs with different contents, as well as understand the mechanism of water sorption. Data analysis shows that the main factors characterizing swelling and water sorption of superabsorbent polymers are the chemisorption of water molecules and the diffusion of water molecules into polymeric networks (Peppas and Brannon-Peppas 1994; Ganji et al. 2010; Sorokin and Lavlinskaya 2021). The type of diffusion can be determined by Ritger-Peppas swelling kinetic model (see the Materials and Methods part) by linear logarithmic graphical processing of the research data. The n exponent shows the diffusion type:

(i)   If $n = 0.5$, this is Case I or Fickian diffusion, characterized by a water diffusion rate that is slower than the polymer relaxation rate;

(ii) If $n = 1.0$, this is Case II diffusion or non-Fickian diffusion, in which the water diffusion rate is faster than the polymer relaxation rate;

(iii) If $0.5 < n < 1$, this is Case III or anomalous diffusion, non-Fickian diffusion, which occurs when the water diffusion and the polymer relaxation rate are about the same (Peppas and Brannon-Peppas 1994; Ganji et al. 2010).

Moreover, values of $n > 1$ and $n < 0.5$ have been observed, which correspond to super case II diffusion and pseudo-Fickian diffusion, respectively. As can be seen, the type of diffusion depends greatly on the nature of the polymers. For example, $n < 0.5$ representing pseudo-Fickian diffusion characterizes ionic dissociated polymers (Kim et al. 2003).

Figure 7 represents the swelling kinetics profiles for all synthesized CMC-SAPs. As can be seen, they are similar regardless of the presence or absence of a plasticizer. The two-stage water adsorption is observed on the curves. The first stage is fast sorption for 30 min; the next is the slow stage till 60 min; and finally, the equilibrium swelling is achieved. It should be noted that CMC-SAPs containing 5% w of DiBu-Suc swell faster compared to samples with 0% w or 2% w, and CMC-SAPs with 10% of DiBu-Suc are characterized by the lowest rate of swelling. This pattern is consistent with our hypothesis concerning the effect of the plasticizer on the superabsorbent matrix which was considered above.
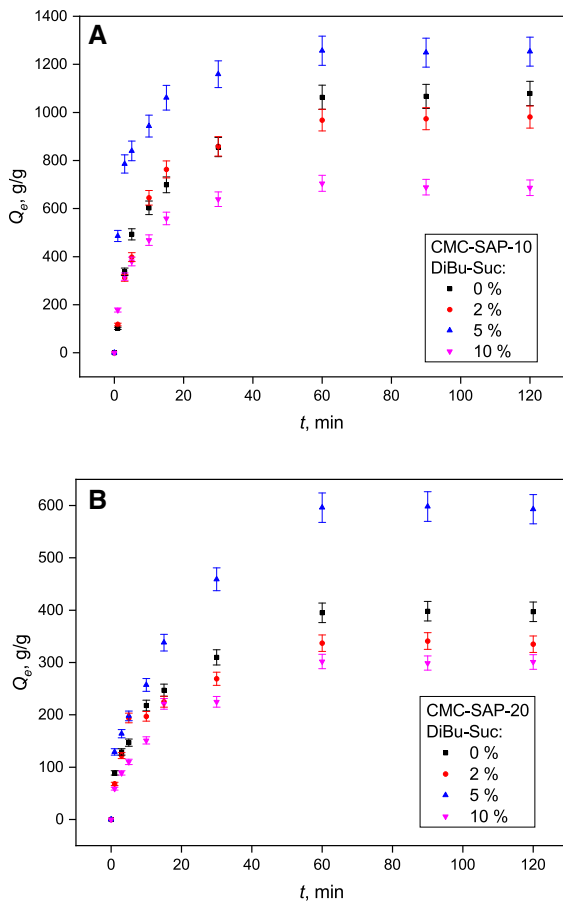
Fig. 7 Swelling kinetics of the CMC-SAPs: **a** CMC-SAP-10;
b CMC-SAP-20

To estimate the influence of DiBu-Suc on the water
sorption mechanism, mathematical kinetic swelling
models were utilized. Data analysis shows that the
most suitable models for SAP swelling investigation
are the pseudo-first-order swelling kinetic model, the
pseudo-second-order swelling kinetic model, and the
Ritger-Peppas model described in the Materials and
Methods part (Fig. 8). The swelling data are processed
by a kinetic model for SAPs without DiBu-Suc and
with 5% w of additive.

The choice of the most appropriate model is carried
out based on the R^2 values of linear approximation of
the models and the non-parametric Chi-square (χ^2)
test. As expected, the swelling kinetics of the CMC-
SAPs without plasticizer is well-fitted to pseudo-
second-order swelling kinetic model (CMC-SAP-
10–0: $R^2 = 0.9981$ and $\chi^2 = 1 < \chi_c^2 = 15.5$;
CMC-SAP-20–0: $R^2 = 0.9957$ and
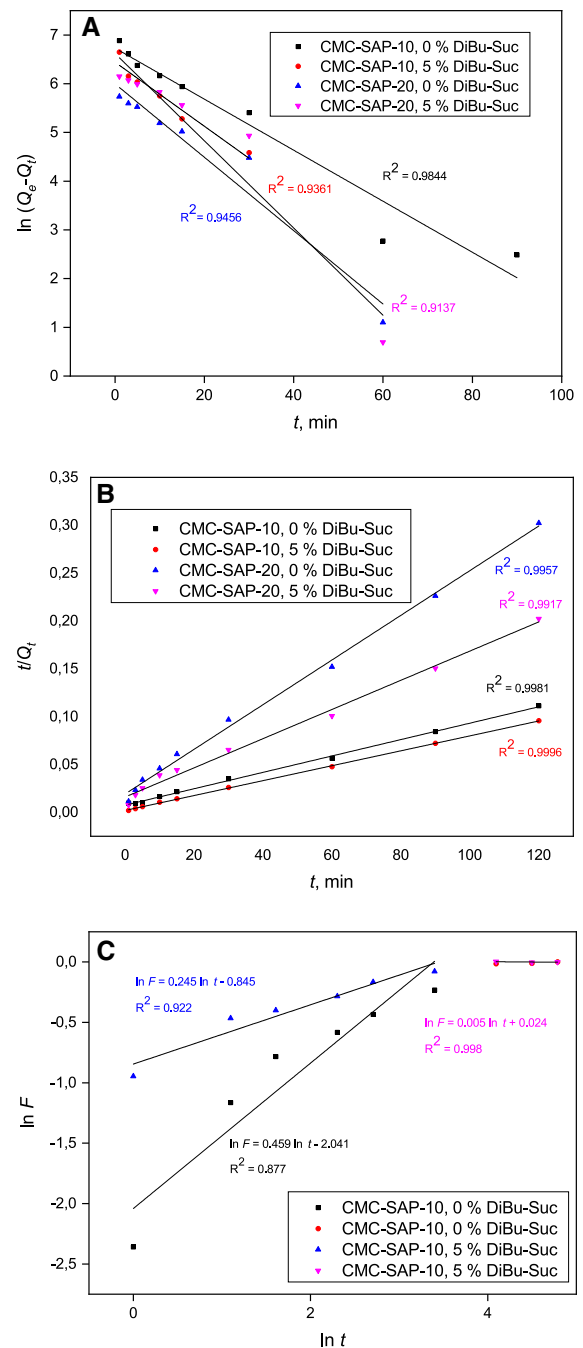
Fig. 8 Swelling kinetic models: **a** pseudo-first-order model;
b pseudo-second-order model; **c** Ritger-Peppas model

$\chi^2 = 0.9 < {} < \chi_c^2 = 15.5$). Also, the data processed
using the Ritger-Peppas model and expressed sepa-
rately for fast and slow absorption stages are charac-
terized by good R^2 values ($R^2 = 0.9980$) for the slow
sorption stage. So, based on the concept of the pseudo-

second-order and the Ritger-Peppas swelling kinetic models, water absorption is controlled by chemisorption at the fast stage, and pseudo-Fickian water diffusion is also important at the slow sorption stage for SAPs prepared without plasticizer. As can be seen, R^2 values obtained for CMC-SAPs with 5% of plasticizer are approximately equal to the ones considered above. So, we can conclude that the presence of dibutyl succinate has no influence on the water sorption mechanism, and it is the same as the one for non-plasticized CMC-SAP.

Water-holding properties are also important for the characterization and application of superabsorbents. Water retention was researched at 80 °C with the use of an automatic moisture analyzer. The weight loss curves for CMC-SAP with 0% w and 5% w of DiBu-Suc are represented in Fig. 9. As can be seen from the data obtained, water retention for all synthesized CMC-SAPs is approximately equal, and the difference between weight loss curves is in the range of experimental errors. Therefore, we can conclude that the plasticizer has no significant influence on water loss at 80 °C.

Figure 10 represents the results of the regeneration study carried out for CMC-SAP-20–0 and CMC-SAP-20–5 expressed as a ratio of the swelling ratio after swelling-deswelling cycle to the initial swelling ratio and denoted as Q_{rev}, %. The loss in the value of the equilibrium swelling ratio does not exceed 10 and 5% for the CMC-SAP-20–0 and CMC-SAP-20–5, respectively. In this case, the experimental error is about 4.5%. Therefore, the swelling possibility of the CMC-SAPs is almost fully retained after 4 swelling-
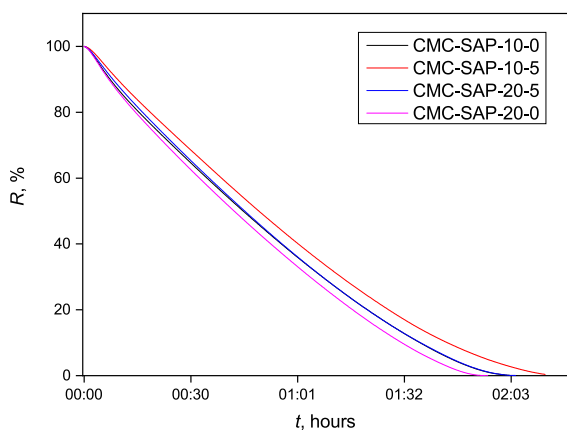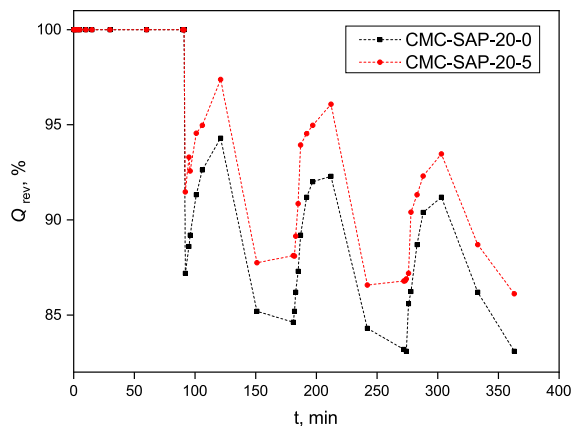

Fig. 10 Regeneration study of the CMC-SAPs

deswelling cycles. This is due to the high stability of the three-dimensional superabsorbent networks resistant to cyclic swelling-deswelling processes. However, the presence of the plasticizer has no sufficient impact on the regeneration process, which is probably due to the significant influence of the temperature on the hydrogen bond formation and destruction (Wei et al. 2015). Consequently, synthesized SAPs are reusable regardless of the presence of dibutyl succinate plasticizer.

Conclusion

The research conducted shows that dibutyl succinate is suitable as a plasticizer for composite superabsorbents enriched in carboxymethyl cellulose sodium salt. The use of 5% w of DiBu-Suc enhances the equilibrium swelling ratio up to 51% due to selective interaction with intramolecular H-bond-forming links, increasing the segmental mobility in the polymeric network and the sterical availability of sorption sites for water molecules. The presence of DiBu-Suc does not change the water absorption mechanism controlled by chemisorption and pseudo-Fickian diffusion of water molecules, and has no significant impact on water retention properties and reusability of the composite superabsorbents.

Fig. 9 Water retention investigation of the CMC-SAPs

Declarations

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