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Wet and dry highly porous cellulose beads from cellulose–NaOH–water solutions: influence of the preparation conditions on beads shape and encapsulation of inorganic particles

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Abstract Wet (swollen-in-water) and dry highly porous cellulose beads were prepared from cellulose–8%NaOH–water solutions by making droplets and coagulating cellulose in water bath. The shape of the beads varied from very flat plates to spheres. The influence of the preparation conditions (cellulose concentration, delay time, bath temperature, and the distance between the pipette and the bath surface) on the shape of the beads is discussed. Higher is the solution viscosity and weaker is the shock of the falling droplet on the bath surface, more spherical are the beads. Gelation of cellulose–NaOH solutions is shown to be a very important factor controlling bead shape. A simple way of encapsulation of various powders in cellulose beads is demonstrated and wet cellulose–inorganic composites were prepared. Highly porous (Aerocellulose) beads carrying encapsulated particles were made by drying coagulated cellulose under CO_2 in supercritical conditions.

Introduction

Cellulose beads are wet or dry particles used for various types of applications, mainly for immobilization, purification, separation, and filtration purposes (see, e.g., [1–3]). Cellulose beads already exist on the market in the form of swollen-in-water particles; they offer high porosity and interesting functional properties due to the large amount of reactive hydroxyl groups. The general principle of making these beads is to dissolve a cellulose derivative (viscose, cellulose esters, or ethers), and then regenerate cellulose in a coagulating bath which chemical composition is tuned to perform "de-derivatisation" (hydrolysis, deacetylation, etc.) [4]. Beads can be made from solutions by either using classical droplet-making machines like atomizers [5] and jet-splitters [6], or, on the laboratory scale, with a syringe or by pressing a solution through a perforated material [2]. To improve some specific absorption properties cellulose can be co-dissolved with some other polysaccharides, like chitin or chitosan [7, 8] or modified to contain charged groups [3]. Mixing cellulose with cellulose esters in a common solvent was reported to influence bead aspect ratio [6].

As mentioned above, cellulose beads, as most of cellulose fibers and films, are made via cellulose derivatisation followed by "de-derivatisation" step. It is of a special interest to be able to make beads through cellulose dissolution in direct solvents. Many are known, such as LiCl/*N*,*N*-dimethylacetamide, ammonium fluorides/dimethylsulfoxide, molten salt hydrates as $LiClO_4 \cdot 3H_2O$ and $LiSCN \cdot 2H_2O$, etc. Most of them possess several undesired properties, like high toxicity, volatility, or high costs limiting their commercial application. *N*-Methylmorpholine *N*-oxide monohydrate (NMMO) is the only cellulose solvent used to produce cellulose fibers on the industrial scale via direct dissolution; however, solution preparation requires rather high energy consumption. Aqueous (7–9)%NaOH solutions, mixed or not with urea or thiourea, have been recently reported as a very promising solvent

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family for direct and easy cellulose dissolution. There are two main problems preventing the use of this solvent for making fibers and films on the industrial scale: (i) cellulose cannot be dissolved at concentrations higher than 7–8% [9, 10] and (ii) solutions are gelling with time and temperature increase [11, 12]. However, for making beads both the problems become much less important: if willing to make porous systems, high cellulose concentration is not the target and gelation, as it will be shown in the following, can be used as a way to modify solution viscosity.

Dry cellulose beads can also be very attractive for various applications as carriers or absorbers and as biodegradable packaging. Drying of wet cellulose beads in the air will lead to the collapse of the pores and channels formed in the swollen regenerated cellulose due to the superficial tension forces. There are two ways to keep the porosity open: freeze-drying and drying in supercritical conditions, e.g., in the supercritical CO_2. It was recently demonstrated that highly porous and light cellulose material called aerocellulose can be obtained via cellulose dissolution in NMMO or in aqueous NaOH [13–15]. Aerocellulose density can be as low as 0.05–0.1 g/cm^3 and specific surface is 200–500 m^2/g.

In this study, we demonstrate that cellulose beads of various shapes, from thin tablets to spheres, can be prepared from cellulose–NaOH–water solutions. We first study the influence of the preparation conditions of the shape of wet particles. Then we demonstrate that aerocellulose beads can be prepared using drying in supercritical CO_2. Finally, we show some examples of encapsulation of inorganic particles into cellulose beads, in the wet and the dry states.

Experimental part

Materials

Microcrystalline cellulose Avicel PH101 (“cellulose” in the following) with degree of polymerization of 170 as given by the manufacturer was purchased from Sigma-Aldrich. NaOH in pellets (97% purity) and acetone (98% purity) were purchased from VWR. Distilled water was used for solution preparation and for coagulation bath. CO_2 for drying in supercritical conditions was supplied by Air Liquide with a purity of 99.9%.

Inorganic particles used were powders of iron from VWR, TiO_2 from Merck, carbon black from Carbon Lorraine and copper from Baudier. The choice of powders was made to demonstrate the possibility of encapsulating of particles of various types and sizes: while iron and copper were large, with particle diameter of 10–150 µm and 50–400 µm, respectively, the size of titanium dioxide and carbon black was below 1 µm but they were assembled in breakable agglomerates.

Methods

Samples preparation

Cellulose–8%NaOH solutions were prepared as described elsewhere [14, 15]. Briefly, an aqueous solution of 12-wt% NaOH was cooled down to −6 °C. Cellulose was swollen in distilled water and kept at 5 °C. 12% NaOH–water and swollen-in-water-cellulose were mixed at −6 °C with a stirring rate of 1000 rpm for 2 h in certain proportions to obtain various cellulose concentrations (wt%) in 8%NaOH–water. Ready solutions were stored at 5 °C to avoid aging. For the preparation of cellulose with encapsulated particles (5 wt%), the latter were added to the ready 5%cellulose–8%NaOH–water solution and stirred for 30 min at 5 °C with the stirring rate of 1000 rpm. The suspension was then subjected to the ultra-sound treatment (Bioblock Scientific device) for a few minutes to improve the dispersion.

Coagulated (or regenerated) cellulose beads of various shapes were prepared using a multi-channel Eppendorf micro-pipette. The pipette reservoir was filled with cellulose–8%NaOH–water solution or 5%particles–5%cellulose–8%NaOH–water suspension which was then dripped into water coagulation bath where complete release of NaOH was attained (see details on coagulation kinetics study in “Results”). First, the correlation between the shape of the beads made from pure cellulose (without particles) and the processing parameters was established. Three parameters were varied: (i) the distance h between the end of pipette and the bath surface, (ii) bath temperature T, and (iii) delay time t that solution was kept at 20 °C in the reservoir. The delay time was used to modify solution viscosity as far as it is known that cellulose–(7–9%)NaOH–water solutions are gelling with time and temperature increase [11, 14, 16]. The results obtained were then used for making spherical beads with encapsulated particles.

To prepare aerocellulose samples, the procedure described in [14, 15] was used, i.e., drying of coagulated cellulose in supercritical CO_2 conditions. Cellulose beads (with and without particles) were washed in acetone to remove water which is not compatible with CO_2. Swollen-in-acetone samples were dried under supercritical CO_2 as described earlier (1-L autoclave, 80 bar, 35 °C) [14, 15]. After depressurisation (4 bar per hour at 37 °C), Aerocellulose beads were extracted and analyzed.

Experimental methods

Gelation of cellulose solutions of various concentrations in 8%NaOH–water was studied using stress-controlled

Bohlin® Gemini rheometer. Dynamic shear experiments were carried out using cone-plate geometry equipped with a Peltier temperature control system. Solutions were introduced on the plate and a layer of low viscosity silicon oil was put around to prevent water evaporation. Gelation of cellulose solutions was studied at 20 °C at frequency 1 Hz and stress 4×10^{-3} Pa ensuring measurements in the linear visco-elastic regime.

Cellulose coagulation in water was studied following the kinetics of NaOH release from the beads into regenerating bath, using ion-selective (Na^+) electrode (Mettler Toledo) coupled with a pH meter from Denver Instruments, as described in [17]. First, a calibration curve of potential (mV) versus known NaOH concentration was built. This calibration was then used to calculate the cumulated amount of NaOH released into the bath from cellulose sample in time. The electrode was inserted in the bath where a few droplets of cellulose–NaOH solution of a known volume were dripped. The volume of the bath was 200 mL; it was large enough to exclude the influence of the final NaOH concentration in the bath at the end of coagulation on the diffusion coefficient (the mean volume of one droplet was about 10–20 mm^3). A magnetic stirrer was used to gently mix liquid in a regenerating bath during NaOH release for concentration homogenization. Each experiment was repeated 3–5 times and the mean value of the diffusion coefficient (see details in the "Results and discussion") was calculated.

The morphology of aerocellulose with and without encapsulated particles was analyzed using scanning electron microscope (SEM) PHILIPS XL30 at the acceleration voltage of 15 kV. Samples were cryofractured and a thin layer of gold was deposited on the surface of the cross section.

Results and discussion

Influence of processing conditions on the shape of coagulated cellulose beads

During the preparation of beads cellulose solution is in the pipette reservoir at room temperature. Because cellulose–(7–9%)NaOH–water solutions are gelling with time and temperature increase [11, 14, 16], solution viscosity may significantly vary in time and influence the final shape of the beads. An estimation of the gelation time is thus needed; it was obtained by measuring the evolution of the elastic G' and viscous G'' moduli as a function of time at 20 °C. In the first approximation the time needed for a the system to reach the gel point t_{gel} is when $G'(t) = G''(t)$ [18]. An example of 5% cellulose solution gelation in time at 20 °C is shown in Fig. 1. It should be noted that the gel formed is weak and can easily be broken under mechanical stresses such as flow [19].

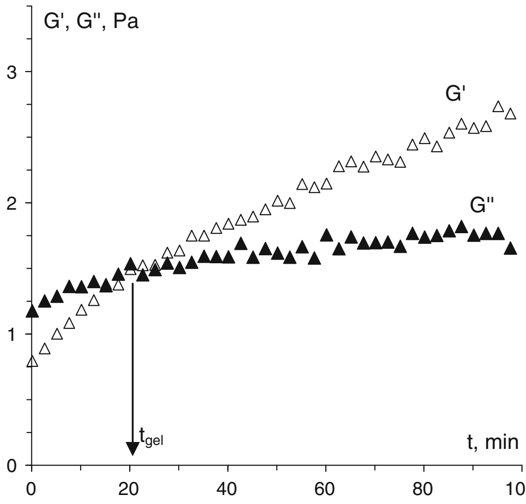
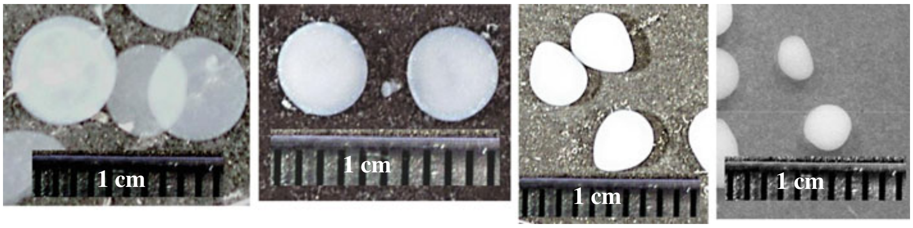


Fig. 1 Evolution of G' and G'' in time for 5%cellulose–8%NaOH-water solution at 20 °C

Cellulose beads were prepared from cellulose–8%NaOH–water solutions of three cellulose concentrations $C = 3$, 4, and 5%. The distance from the end of pipette to the bath surface was $h = 10$, 5, and 0.5 cm; delay time at which solution was kept in pipette reservoir was $t = 0$, 15, and 60 min and bath temperature was $T = 20$ and 40 °C. These parameters were varied one after another keeping the others constant.

Beads of various shapes were obtained, from very thin, almost transparent disk-like, to spherical. In overall, about few thousand beads were prepared and analyzed visually. In order to correlate the processing conditions and bead shape the latter were arbitrary divided into four categories (Fig. 2) with several hundreds belonging to each category and the sizes of about 30 beads of each category measured: (a) very flat "plates" with the thickness being at least 20 times smaller than the diameter, (b) "disks" with the thickness being about 10 times smaller than the diameter, (c) "droplets" with the thickness being about 5 times smaller than the diameter and with the shape of droplets, and (d) "spheres" with the thickness being almost the same as diameter. The shape of the beads corresponding to various preparation conditions is presented in Table 1 where each of the four shapes is coded with a symbol for clarity.

Table 1 shows that for a given coagulation bath temperature higher is solution viscosity (which depends both on cellulose concentration and on delay time controlling gelation), more spherical are the beads obtained. For example, 5% cellulose solution kept in the reservoir for 1 h overpassed the gel point: despite the fact that the weak gel is broken when pushed out from pipette, solution



« plates » (X) « disks » ([]) « droplets » (Δ) « spheres » (O)

Fig. 2 Wet (swollen-in-water) cellulose beads of various shapes

Table 1 Correlation between beads shape (see Fig. 2 for *symbols*) and the preparation conditions: cellulose concentration C, delay time t, and distance $h_1 = 10$ cm, $h_2 = 5$ cm, and $h_3 = 0.5$ cm

Bath temperature (°C)	C (%)	$t = 0$ min			$t = 15$ min			$t = 60$ min		
		h_1	h_2	h_3	h_1	h_2	h_3	h_1	h_2	h_3
20	3	X	X	X	X	X	X	X	X	X
	4	X	X	X	X	X	X	[]	[]	[]
	5	X	X	X	X	X	[]	[]	Δ	Δ
40	3	X	X	X	X	X	X	X	X	X
	4	X	X	[]	X	X	[]	[]	[]	Δ
	5	X	X	[]	[]	Δ	Δ	O	O	O

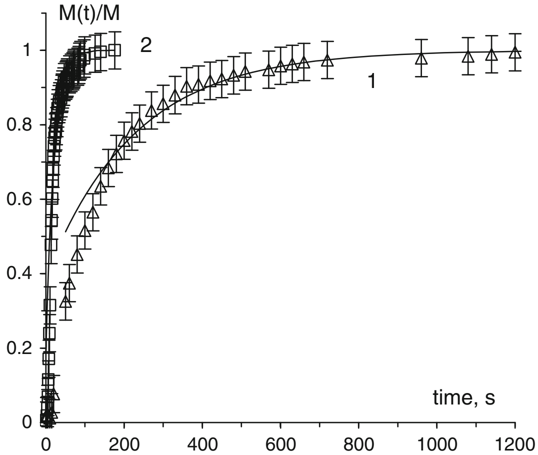


Fig. 3 Relative cumulated amount of NaOH released into a bath as a function of time for cellulose spheres coagulating in water bath at 42 °C (*1*), and flat plates in a bath at 20 °C (*2*). *Solid lines* correspond to late-time approximation

viscosity is much higher than the one at $t = 0$ and elastic properties are dominating viscous ones, helping resisting the shock the droplet undergoes when meeting bath surface. The distance h is also important: smaller it is, more spherical is the shape because of the decrease of the shock on the surface. Interestingly, bath temperature also plays a significant role in the determination of the shape of the beads: higher is the bath temperature, more spherical is the shape. The reason is that at 40 °C gelation is quasi-instant, within a few seconds [14]. It occurs at the same time as cellulose coagulation, both phenomena starting on the sample surface and thus "reinforcing" the bead. Droplets made from 5% cellulose solution, being "pre-gelled" after 1-h delay, are additionally "solidified" at 40 °C thus helping keeping the spherical shape.

In overall, the results obtained are qualitatively predictable: droplet deformation depends on the ratio of solution to external medium viscosity, the interfacial tension and droplet size. In our case, the mechanical shock due to the meeting of the droplet with the bath surface should also be considered. As far as the interfacial tension and droplet size do not vary, only solution viscosity and shock on the bath surface remain to be considered. Thus to obtain spherical beads the shock should be minimized and viscosity maximized. By controlling the processing conditions, various shapes of coagulated bead-like cellulose, from very flat to spherical, can be obtained.

To study the kinetics of NaOH release from the samples of different shapes is of interest in the view of predicting time needed for complete cellulose coagulation. As shown in [15, 17], cellulose coagulation is a diffusion-controlled process: Na$^+$ release into regenerating bath is described by Fick law. We studied NaOH release from 5%cellulose–8%NaOH–water solutions for two limiting cases: spheres in a bath at 42 and 53 °C and flat "plates" in a bath at 20 and 30 °C. The principles of the measurements and of results analysis are described in detail [15, 17]. Cumulated amount of NaOH released into a bath, $M(t)$, is measured as a function of time t. An example of a relative cumulated mass $M(t)/M$, where M is the mass of released substance at the end of regeneration, is shown in Fig. 3 for spheres coagulating at 42 °C and plates at 20 °C.

The time of complete cellulose coagulation (or regeneration), i.e., when all NaOH is released into the bath, is several times lower for thin samples as compared with the spherical ones, despite that thin plates shown here were regenerated at a lower temperature than the spheres. The overall time needed to regenerate cellulose depends on cellulose concentration, sample shape, and bath temperature. An adequate way to understand and predict cellulose coagulation kinetics in a sample of any shape at any temperature at a fixed cellulose concentration is to determine Na$^+$ diffusion coefficient, D. As demonstrated in [15, 17], early time, half-time, and late-time approximations can be used to calculate D from the experimental data

Table 2 Approximations used to calculate the diffusion coefficient of a substance released from a sphere and an infinite plane

	Early time: $0 \leq \frac{M(t)}{M} \leq 0.4$	Half-time: $\frac{M(t)}{M} = 1/2$	Late-time: $0.4 \leq \frac{M(t)}{M} \leq 1$
Sphere with radius r	$\frac{M(t)}{M} = 6\left(\frac{Dt}{\pi r^2}\right)^{1/2} - \frac{3Dt}{r^2}$	$D = \frac{0.031}{(t/r^2)_{\text{at}\, M(t)/M=0.5}}$	$\frac{M(t)}{M} = 1 - \frac{6}{\pi^2}\exp\left(\frac{-\pi^2 Dt}{r^2}\right)$
Infinite plane with thickness $2l$	$\frac{M(t)}{M} = 4\left(\frac{Dt}{\pi l^2}\right)^{1/2}$	$D = \frac{0.049}{(t/l^2)_{\text{at}\, M(t)/M=0.5}}$	$\frac{M(t)}{M} = 1 - \frac{8}{\pi^2}\exp\left(\frac{-\pi^2 Dt}{l^2}\right)$

Table 3 Diffusion coefficients, mm^2/s, calculated for cellulose spheres and thin plates prepared from 5%cellulose–8%NaOH–water solutions with three approximations

	T (°C)	Early time	Half time	Late time	Mean value
Sphere, mean $r = 1.25$ mm	42	$(7.5 \pm 0.8) \times 10^{-4}$	$(5.7 \pm 0.6) \times 10^{-4}$	$(7.3 \pm 0.7) \times 10^{-4}$	$(6.9 \pm 0.7) \times 10^{-4}$
	53	$(1.8 \pm 0.2) \times 10^{-3}$	$(1.4 \pm 0.1) \times 10^{-3}$	$(1.7 \pm 0.2) \times 10^{-3}$	$(1.7 \pm 0.2) \times 10^{-3}$
Flat plate, mean $2l = 0.3$ mm	20	$(1.3 \pm 0.1) \times 10^{-4}$	$(8.8 \pm 0.9) \times 10^{-5}$	$(1.1 \pm 0.1) \times 10^{-4}$	$(1.1 \pm 0.1) \times 10^{-4}$
	30	$(1.4 \pm 0.1) \times 10^{-4}$	$(1.5 \pm 0.2) \times 10^{-4}$	$(1.2 \pm 0.1) \times 10^{-4}$	$(1.3 \pm 0.1) \times 10^{-4}$

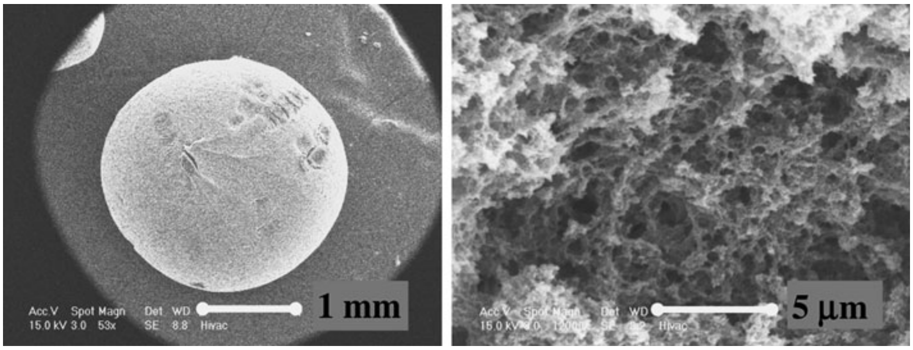


Fig. 4 Aerocellulose bead obtained from 5%cellulose–8%NaOH–water solution

$M(t)/M$ vs. t. The expressions are shown in Table 2 for two shapes of the samples studied, spheres and thin plates, the latter analyzed with an infinite plane approximation.

Na$^+$ diffusion coefficients calculated for cellulose spheres and thin plates within each approximation are shown in Table 3. As far as results presented here are for fixed cellulose concentration, 5%, Na$^+$ diffusion coefficients depend only on temperature and increase with temperature increase. The results obtained allow an estimation of cellulose overall coagulation time: e.g., it will take a few days to completely regenerate in water at room temperature a spherical bead with the radius of 1 cm made from 5%cellulose–8%NaOH–water.

Wet cellulose beads can be, in general, prepared using industrial bead-making technologies as atomizers, air-splitters, or jet-cutters. The gelation of cellulose–NaOH solutions can be an interesting way to tune the shape of the beads without increasing cellulose concentration.

If drying swollen-in-water beads in the air, compact particles will be obtained as it was shown for cellulose beads made from viscose [5]. To make dry light and highly porous cellulose, like aerocellulose [14, 15], wet samples should be dried under supercritical CO$_2$. We used this way of drying to prepare aerocellulose beads, see details in "Methods". SEM images of an aerocellulose bead are shown in Fig. 4 at two scales. A successful application of a jet-cutting method for making aerocellulose beads was

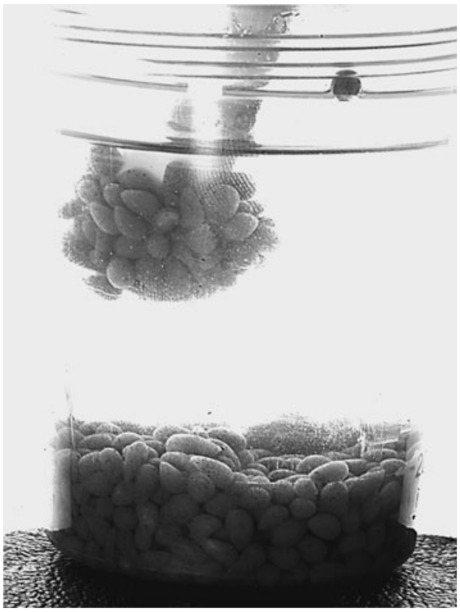


Fig. 5 Magnetic iron-encapsulated wet cellulose beads

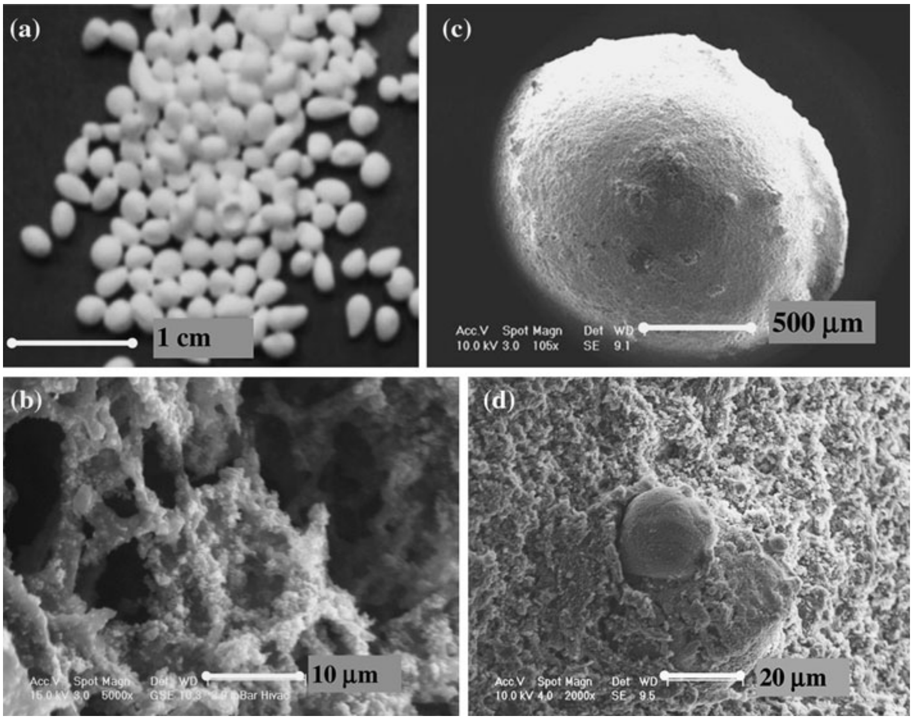


Fig. 6 Photos and SEM images of TiO_2-encapsulated (**a**, **b**) and iron-encapsulated (**c**, **d**) aerocellulose beads

demonstrated in the frame of "Aerocell" EC 6th framework project.

Cellulose with encapsulated particles

Various solid particles were mixed with 5%cellulose–8%NaOH–water solutions as described in "Methods". Beads were then prepared using the same procedure as described above for pure cellulose solutions. During coagulation and washing in acetone all particles remained inside the beads (no sediment in regenerating bath) except carbon black which was partly released. The shape of the beads was ellipsoidal because of the increase of suspension viscosity. An example of wet regenerated cellulose beads with encapsulated iron is shown in Fig. 5; the beads possess magnetic properties.

The examples of aerocellulose beads with encapsulated particles are shown in Fig. 6. Similar results were obtained for other encapsulated particles. These images demonstrate the feasibility of making highly porous beads with various types of encapsulated particles that can be chosen according to the desired application.

Conclusions

Wet and dry cellulose beads of various shapes, from very thin plates to spheres, were obtained from cellulose–8%NaOH–water solutions. The main parameters influencing the shape of the beads are solution viscosity and the strength of the shock of droplet on the surface of the coagulation bath. Various inorganic powders were used to demonstrate the possibility of particles encapsulation into cellulose and aerocellulose beads. The method used is simple and allows the preparation of wet and dry highly porous functionalized cellulose beads with properties tuned for desired applications (medical, cosmetic, filtration, etc.).

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