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Cellulose gel dispersion: From pure hydrogel suspensions to encapsulated oil-in-water emulsions

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ABSTRACT

Cellulose hydrogel particles were fabricated from molecularly-dissolved cellulose/IL solutions. The characteristics of the formed hydrogels (cellulose content, particles' size and porosity) were determined as a function of cellulose concentration in the precursor solutions. There is a significant change in the hydrogel structure when the initial cellulose solution concentration increases above about 7–9%wt. These changes include increase of the cellulose content in the hydrogel, and decrease in its pore size. The finest cellulose particle dispersions can be obtained using low concentration cellulose/IL solutions (cellulose concentration in dispersion less than 2%wt.) or hydrogels (concentration less than 1%wt.) in a dispersing medium consisting of IL with no more than 20%wt. water. Stable paraffin oil-in-water emulsions are achieved by mixing oil and water with cellulose/IL solutions. The optimal conditions for obtaining the finest particles (about 20 μm in diameter) are attained using cellulose solutions of concentration between 0.7 and 4%wt. at temperature of 70 °C and oil/cellulose mass ratios between 1 and 1.5.

1. Introduction

It is not necessary to describe once again the intriguing structure and properties of cellulose – one of the most inexhaustible natural polymers, which has long been used by mankind for a variety of purposes. Much scientific research has been devoted to this topic [1–3]. Nevertheless, much attention is devoted recently to studies of dissolution and subsequent regeneration of cellulose in ionic liquids (IL) [4–9] and, in particular, their mixtures with polar organic cosolvents [10–14].

Cellulose gels are fabricated directly from native cellulose via cellulose dissolution and subsequent regeneration with water (hydrogels), ethanol, acetone or other polar non-solvents (lyogels). Optimally, the cellulose molecules forming the hydrogel possess the same degree of polymerization as those initially dissolved. Hydrogels are three-dimensional network structures formed by physically cross-linked cellulose molecules containing large amount of adsorbed water (i.e. physically bonded at sorption sites of the cellulose molecules) and more mobile trapped water (i.e. captured into the gel porous network, but less strongly bonded to cellulose) [15]. Cellulose hydrogels have many favorable properties such as hydrophilicity, biodegradability, biocompatibility, transparency, low cost and non-toxicity. Therefore, they have wide applications in tissue engineering, controlled delivery system, sensor, water purification and more [16–18]. Subsequent drying of the lyogels induces hornification effects due to irreversible aggregation. It was concluded that porosity and crystallinity are more tunable in cellulose hydrogels coagulated in water than in corresponding lyogels coagulated in alcohols [19].

Cellulose hydrogels serve as a starting material for preparation of cellulose beads. These are spherical particles with diameters in the micro- to millimeter scale, which are used in many advanced applications, such as chromatography over solid supported synthesis, protein immobilization and controlled drug delivery. Shaping of hydrogels into spherical particles is realized by various methods: dropping, jet cutting, spinning drop atomization, spraying, ultrasonic dispersion techniques, etc. [20]. The obtained cellulose particles are almost the same size as the original droplets, indicating a microporous structure of the cellulose particles with a large content of the dispersing medium [21].

As can be found in the literature, many water-soluble polysaccharides such as modified starch, dextran, agarose, chitosan, hydroxypropyl- or methyl-cellulose, can be used for the oil (lipid) emulsification. Even after drying and subsequent rehydration of these emulsions, their internal structure is reserved [22,23]. Polysaccharides-lipid dispersions are known for their applications in food, cosmetics, and medical fields [24].

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Our recent studies have shown that cellulose chains are molecularly dissolved in an ionic liquid and its solvent mixture with certain polar organic solvents, forming a true solution [14]. This is evidenced by the structural information on the dissolved chains (average molecular weight $\sim 5 \times 10^4$ g/mol; gyration radius ~36 nm, persistence length ~4.5 nm), which indicates the absence of significant aggregation of the dissolved chains, and the calculated value of the second virial coefficient $\sim 2.45 \times 10^{-2}$ mol ml/g^2. Due to their molecular dissolution, the cellulose chains in hydrogels formed by regeneration of these solutions maintain an amorphous structure. This phenomenon is confirmed by X-ray diffraction patterns which indicate that the hydrogel formed by regeneration of cellulose solutions is indeed in the amorphous state [25]. Furthermore, it was reported that the cellulose solutions or suspensions of regenerated hydrogel particles can be used for emulsification oil in water, by forming a stabilizing coating for oil-in-water (O/W) and water-in-oil (W/O) emulsions without additional surfactants [14,25]. It was noted that when the crystals of native cellulose are disrupted, and cellulose chains can act as a molecular surfactant and can form a stable aqueous dispersion when interacting with single walled carbon nanotubes [26]. We suggested that these emulsification abilities is directly related to the specific amphiphilic character of the cellulose molecules [25], as is discussed in recent scientific literature [27–34].

The objective of this study is to evaluate the relationship between the concentration of molecularly-dissolved cellulose in the precursor solution, the characteristics of the hydrogel formed by their regeneration (cellulose content, size and porosity of suspended hydrogel particles), and the emulsification ability of such precursor solutions, by forming a stable encapsulating layers on dispersed oil drops. These investigations give the necessary knowledge for the successful production of the natural cellulose coatings with controlled molecular permeability for the drug delivery systems and other biomedical applications.

2. Experimental

2.1. Materials, equipment and methods

Microcrystalline cellulose powder (Avicel®) with particle size in the range of 70–250 μm and the ionic liquid 1-ethyl-3-methylimidazolium acetate (EMIMAc) of 90% purity were supplied by Sigma–Aldrich Co. EMIMAc and cellulose were dried in a vacuum oven at 60 °C at 0.26 kPa for at least 24 h before use. Light paraffin oil (a mixture of alkanes with chain length in the range of 8–11 carbon atoms) and dichloromethane (DCM) were supplied by Sigma–Aldrich Co., and used without additional treatment.

Two devices were used for dispersion and emulsification processing: an Ultrasonic cell disruptor 2000U (Ultrasonic Power Corp., USA) equipped with a finger-like tip at frequency of 20 kHz and capacity 200 W and mechanical homogenizer IKA® T-18 Ultra-Turrax® (IKA Works Inc., USA). A Mastersizer 2000 instrument (Malvern Co. Ltd., UK) was used to measure the particle size and distribution. The size range measured by this apparatus is 20 nm–2 mm. In all measurements the background was taken as the respective IL/water mixture as that of the measured solution. Three–five repeated measurements were performed on each sample; the standard deviation of the average measurement does not exceed 30%.

For structure and morphology investigation of the cellulose hydrogel with different cellulose concentrations, a cryogenic high-resolution scanning electron microscope (cryo-HRSEM) Ultra Plus Gemini (Zeiss Co. Germany) was used. Cryo-HRSEM specimens of cellulose hydrogels with different cellulose concentrations (2, 6, 8, 12 and 18%wt.) were prepared in a controlled environment vitrification system (CEVS) at room temperature and ambient conditions and were vitrified with liquid ethane. The cryo-HRSEM gel images were processed using the scientific image analysis program ImageJ®, included in the standard software of the cryo-HRSEM. It was used for the analysis at least two images for each gel concentration, in each of which at least three different sites were processed. The average pore diameter was calculated using at least 40 pores on each site. For all measurements the average pore diameter standard deviation does not exceed 30%. Small angle X-ray scattering (SAXS) was performed using a small-angle diffractometer (Molecular Metrology SAXS system with CuK_α radiation (wavelength ~0.154 nm) from a sealed microfocus tube (MicroMax-002 + S, two Göbel mirrors, and three-pinhole slits). The resolution of the SAXS system is about 3 nm. The examined gel was sealed in a flat mica-covered cuvette (1.3 mm thick, Linkam Inc.).

Cellulose dissolution was realized by adding Avicel® powder to EMIMAc (20–40 ml), preheated to 80 °C under mild stirring. To accelerate the dissolution process, its stability and uniformity, the cellulose powder was preliminary impregnated with a small amount of DCM (~10%, w/w) [25]. The cellulose/DCM mixture was added in small aliquots to the hot IL solvent during which DCM was rapidly volatilized from the solution. Throughout the exothermic dissolution process the temperature was monitored taking care that it does not exceed 120 °C to limit cellulose decomposition. The investigated range of cellulose concentration was 2–18%wt. The dissolution process was implemented using mild stirring with a magnet stirrer for solutions of 2–10%wt. and by a mechanical impeller for more viscous solutions (12–18%wt.).

Cellulose regeneration was implemented by gentle addition of water at room temperature to the hot cellulose/IL solution (80 °C; solution/water volume ratio 1:3). This was done without stirring in order to prevent any damage to the hydrogel structures. The obtained cellulose hydrogel was rinsed with distilled water to remove IL traces, until its complete removal (electrical conductivity of effluent became below 0.5 mS/cm, which is close to the conductivity of deionized flushing water).

The fine dispersions of hydrogel particles were prepared using two different procedures. In the first, cellulose/IL solutions at different concentrations were gradually added to a dispersing medium composed of IL/water mixtures at different ratios. Alternatively, the regenerated hydrogel was dispersed at similar IL/water mixtures by mechanical homogenization (~15 min, stirring rate 700 rpm), followed in some cases by sonication (~45 min). In both cases temperature was controlled.

Cellulose encapsulation of oil-in-water emulsions was carried out using cellulose/IL solutions, mixed with preheated batches of light paraffin oil/water dispersions. All components had the same temperature; they were subjected to the mechanical stirring using the IKA homogenizer (15 min) with continuous addition deionized water (about 2 ml/min) up to fivefold increase in the mixture volume. In some cases subsequent ultrasonic treatment of the emulsions (for 45 min) was carried out [25].

3. Results & discussion

3.1. Specific structural features of cellulose hydrogels

The cellulose content in the regenerated hydrogels obtained from cellulose solutions in IL of different initial concentrations was investigated by drying the hydrogel samples in a vacuum oven at 60 °C and 0.26 kPa for 6 h. The dependences of the hydrogel cellulose content and the pore size of its network (measured by cryo-HRSEM imaging, as shown in Fig. 1b and c), on the initial cellulose solution concentration, are shown in Fig. 1a. As can be seen, the hydrogel cellulose network becomes denser and less open,

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