Dispersion systems based on nanoparticles

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Doctoral Thesis Summary

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Disperzní systémy na bázi nanočástic

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CONTENT

ABSTRACT

Colloidal systems play an important role in various industrial fields. As these systems are usually unstable, considerable effort is devoted to their stabilization by suitable stabilizers. A wide range of substances is used for this purpose; however, due to the growing need to protect the environment, attention is increasingly focused on materials from renewable natural sources and materials showing biocompatibility with living systems. In this context, nanocellulose is considered one of the new potential candidates for the development of materials and products towards a more sustainable future. With the growing development of nanotechnology, nanocellulose has emerged as a very interesting material. Due to its remarkable properties, ecological nature, and easy availability, it is considered one of the most important "green" materials of the modern age.

Following the issue of stabilization of dispersion systems, the doctoral thesis is devoted to cellulose nanoparticles and their ability to stabilize colloidal dispersions. Specifically, two types of dispersion systems are studied here. The first type are classical dispersions, where the Pickering emulsions composed of a combination of titanium dioxide particles and cellulose nanoparticles are studied. Such systems could be used, for example, in UV protection products. The second type of studied systems includes conducting polyaniline-based colloidal dispersions prepared by polymerization in the presence of two types of cellulose nanoparticles, namely cellulose nanocrystals or nanofibers. In the next step, the work focused on the use of these systems for the preparation of Pickering emulsions and thin conducting films with potential applications in biomedicine.

Key words: *nanocellulose, polyaniline, Pickering emulsions, colloidal dispersion, stabilization*

ABSTRAKT

Koloidní systémy hrají významnou roli v řadě průmyslových odvětví. Jelikož se obvykle jedná o nestabilní systémy, je značné úsilí věnováno jejich stabilizaci pomocí vhodných stabilizátorů. Ke stabilizaci koloidních systémů lze použít širokou škálu látek, avšak vzhledem k rostoucím potřebám společnosti a nutnosti ochrany životního prostředí se pozornost stále více upírá na materiály z obnovitelných přírodních zdrojů a na materiály vykazující biokompatibilitu s živými systémy. V této souvislosti je nanocelulóza považována za jeden z nových potenciálních kandidátů pro vývoj materiálů a produktů směrem k udržitelnější budoucnosti. S rostoucím rozvojem nanotechnologií se nanocelulóza ukázala jako velmi zajímavý materiál. Díky svým pozoruhodným vlastnostem, ekologické povaze a snadné dostupnosti je považována za jeden z nejvýznamnějších „zelených“ materiálů moderní doby.

V návaznosti na problematiku stabilizace disperzních systémů se dizertační práce věnuje nanocelulózovým částicím a jejich schopnosti stabilizovat koloidní disperze. Konkrétně jsou zde studovány dva typy disperzních systémů. Prvním typem jsou klasické koloidní disperze, kde je studována příprava Pickeringových emulzí využívající ke stabilizaci kombinaci částic oxidu titaničitého a částic nanocelulózy. Takové systémy by mohly najít uplatnění například v přípravcích na ochranu proti UV záření. Druhý typ studovaných systémů zahrnuje vodivé koloidní disperze na bázi polyanilinu připravené polymerací ve vodném prostředí využívající ke stabilizaci dva typy nanocelulózových částic, a to celulózové nanokrystaly nebo nanofibrily. V dalším kroku se práce soustředila na využití těchto systémů pro přípravu Pickeringových emulzí a tenkých vodivých filmů s potenciálními aplikacemi v biomedicíně.

Klíčová slova: *nanocelulóza, polyanilin, Pickeringovy emulze, koloidní disperze, stabilizace*

1. BACKGROUND

The field of nanotechnology is one of the most exciting and dynamic areas of science today. Nanotechnology deals with the production and use of materials of different types at the nanoscale level in various fields, such as medicine, the automobile industry, electronics, energy storage, catalysis, cosmetics, biotechnology, and environmental applications [1–3]. Nanomaterial is currently defined by the European Commission (2011/696/EU) as a *natural, incidental, or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm – 100 nm.* Nanoparticles (NPs) are the basic component in the production of nanostructures [4], and according to the International Organization for Standardization (ISO) (ISO/TS 80004-2:2015), they are defined as an object with three dimensions below 100 nm. However, the definitions of nanomaterials and nanoparticles are not completely uniform. They vary from organization to organization and continue to be an area of active scientific and political debate [4–6]. Because of their size, NPs have high surface-to-volume ratios, so they exhibit very specific physical and chemical properties which make them suitable candidates for various applications [1]. Compared to conventional materials, the properties of nanoscale materials can impart new material properties and biological behaviour [7,8]. In recent years, more attention has been focused on nanoscale bio-based materials. In the field of nanotechnology, nanocellulose has emerged as a highly interesting biomaterial and is considered one of the most promising materials [9].

The primary goal of this doctoral thesis is to investigate the ability of cellulose nanoparticles, whether they are natural or modified, to stabilize colloidal dispersions, as well as to research systems derived from them. Thus, this work advances the knowledge of the behaviour of cellulose nanoparticles, a topic that is currently being investigated by many scientists.

2. COLLOIDAL DISPERSIONS

Disperse system refers to a two-phase system with one substance (dispersed phase) distributed throughout the second substance (continuous phase). There are two main approaches to the classification of dispersion systems: 1) the nature of the dispersed and continuous phases (Tab. 1), and 2) the size range of dispersed particles/droplets [10,11]. As far as particle/droplet size is concerned, dispersions are generally classified as molecular dispersions (< 1 nm), colloidal dispersions (1 nm − 1μm), and coarse dispersions (> 1μm) [12]. The latter classification is important due to the different behaviour of these systems in a given colloidal range.

Table 1 Types of disperse systems [11].

Dispersed phase	Dispersion Medium	Type
Solid	Liquid	Suspension
Liquid	Liquid	Emulsion
Liquid	Solid	Gel
Liquid	Gas	Aerosol
Gas	Liquid	Foam
Solid	Solid	Composite

2.1 Pickering emulsions

A special type of emulsions are the Pickering emulsions (PE), which use solid particles for the stabilization of emulsion droplets. Various particles, such as starch [13,14], silica [15,16], calcium carbonate [17,18], titanium dioxide [19–21], or organic particles [22] can be used to stabilize Pickering emulsions, and their diversity allows the preparation of emulsions with custom features and functions [23]. In practice, effective Pickering stabilization can be achieved using particles whose average size is at least an order of magnitude smaller than the size of the emulsion droplets. For this reason, nanoparticles are needed to stabilize submicrometer droplets [24].

Compared to other stabilization mechanisms, stabilization by solid particles offers many advantages, such as high stability against coalescence and Ostwald ripening [14]. Pickering emulsions are also characterized by low toxicity and excellent skin compatibility compared to conventional surfactant-stabilized emulsions, which sometimes show negative effects on the skin, often demonstrated by their irritation. In many cases, Pickering emulsions are biologically compatible and environmentally friendly [25–27]. These special types of emulsions are considered promising systems in the field of biomedicine, food, cosmetics, and many others [28]. Moreover, Pickering emulsions, which are sensitive to external stimuli (e.g. temperature, pH, or light), have an interesting use [26].

3. NANOCELLULOSE

Cellulose is the most abundant renewable polymer consisting of glucose units linked by β-(1-4) glycosidic bonds [29,30]. In recent years, interest has focused on nanocellulose, especially for its interesting properties and a wide range of possible applications [9]. Cellulose can be converted to nanocellulose using various approaches, such as mechanical, chemical, and enzymatic treatments [31]. Three main types of nanocellulose include, (1) cellulose nanocrystals (CNC) also called nanocrystalline cellulose, cellulose (nano) whiskers, rod-like cellulose microcrystals; (2) cellulose nanofibrils (CNF) also known as nanofibrillated cellulose (NFC), microfibrillated cellulose (MFC), cellulose nanofibers; and (3) bacterial cellulose (BC) or microbial cellulose [32]. The properties of nanocelluloses mainly depend on fabrication route, processing conditions, the source of cellulose, and on the subsequent functionalization of the surface [33,34]. Attractive properties of nanocellulose include outstanding mechanical properties, biocompatibility, adaptable surface chemistry, great optical properties, and primarily compatibility with a broad range of materials such as polymers, proteins, and/or cells. Due to these properties, nanocellulose has an enormous potential in many applications [35]. In this context, the use of nanocellulose in the field of biomedicine is particularly interesting. Because some tissues respond to electrical fields and stimuli [36], conductivity is considered an important material characteristic in biomedical applications. Therefore, it could be advantageous to combine biocompatible nanocellulose with electrically conducting polymers in the development of biomedical materials. In addition to these applications, the use of nanocellulose in cosmetics is also interesting. Especially in the case of topical applications, nanocellulose can be used as carriers for UV-blocking products [37].

3.1 Cellulose nanocrystals

Cellulose nanocrystals (CNC), as illustrated in Fig. 1a, have a rod-shaped structure (length ~ 100–250 nm and diameter ~ 5–70 nm) that tapers at the end of the crystal. During CNC production, the amorphous regions of cellulose are removed which leads to highly rigid nanomaterial with high crystallinity [38]. CNC can be prepared by hydrolysis with sulfuric or hydrochloric acids or *via* oxidation with strong oxidizing agents such as 2,2,6,6-tetramethylpiperidine-1-oxy radicals (TEMPO) or ammonium persulfate (APS). During the hydrolysis with sulfate acid, charged sulfate ester groups ($-OSO_3H$) are introduced onto the cellulose surfaces, which contribute to the electrostatic stabilization of the CNC in an aqueous suspension. Similarly, hydrochloric acid can be used [39–42]. TEMPO-mediated oxidation uses harmful agents such as hydrazine or sodium borohydride ($NaBH_4$), which show toxicity and generate a lot of chemical waste [43]. A more energy-efficient method for obtaining CNC is based on the oxidation of cellulose materials with APS, which exhibits low long-term toxicity, high solubility in water, and a favourable price.

The preparation of highly crystalline CNC according to Leung et al. [44] *via* oxidation with APS produces nanocellulose with –COOH groups at the surface and higher thermal stability than traditional hydrolysis-produced CNC [45]. Due to the carboxyl groups on the CNC surface, the nanocellulose prepared by this process is referred to as carboxylated cellulose nanocrystals (cCNC) [43].

3.2 Cellulose nanofibers

Cellulose nanofibers (CNF)[1], also called microfibrillated cellulose (MFC) or nanofibrillated cellulose (NFC), excels in low-density and high mechanical properties [46]. It contains very long cellulose nanofibers with a length of ~ 1–10 μm and a diameter of ~ 5–60 nm (Fig 1b). The longer fibers of the CNF compared to the shorter rod-like CNC are due to the presence of an amorphous region in the CNF. CNFs can be produced in several different ways [38] such as high-pressure homogenization or other mechanical processes, which can be used individually or in combinations. However, the disadvantage of the process is the high consumption of energy. In this context, some pretreatments of the starting material are included in the CNF manufacture to reduce the size of fibers before homogenization [46].

3.3 Bacterial cellulose

Bacterial cellulose (BC) is an extracellular polysaccharide produced by some bacteria such as the genera *Gluconacetobacter* (formerly *Acetobacter*), *Agrobacterium, Aerobacter, Achromobacter, Azotobacter, Rhizobium, Sarcina,* and *Salmonella*. BC has a high purity and exhibits a higher degree of polymerization and crystallinity resulting in a very high elastic modulus [47]. BC shows a characteristic ribbon-like nanofibril structure (Fig. 1c) with a diameter of ~ 20–100 nm [38,47]. Considering the challenging large-scale production and commercialization of the BC, the use of CNC or CNF appears to be a more attractive alternative [48,49].

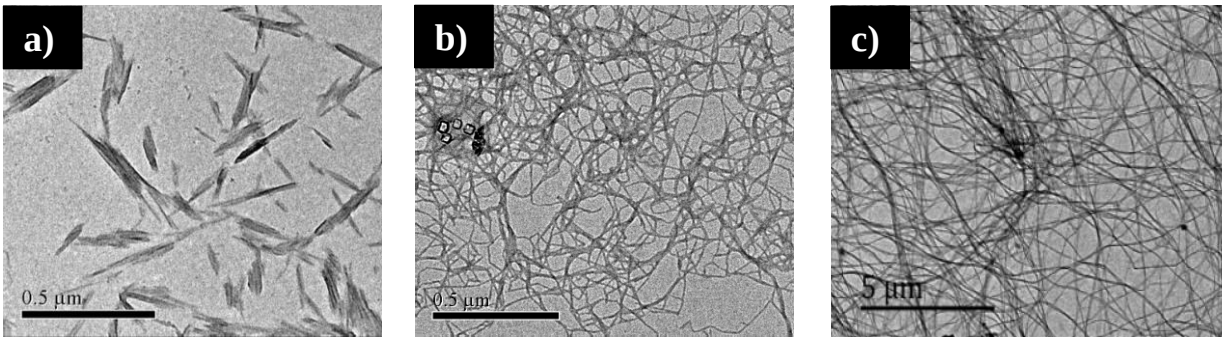


Figure 1 TEM images of (a) CNC (b) MFC and (c) BC [50].

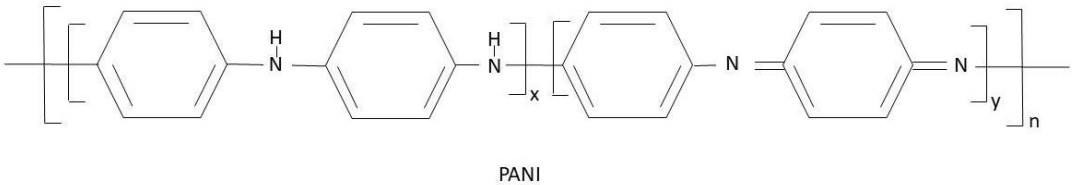
[1] *Cellulose nanofibers are abbreviated differently in literature – we adopted CNF in this thesis.*

4. CONDUCTING POLYMERS

The term conducting polymer (CP) refers to a large class of materials that can conduct electrical charge [51]. The electrical conductivity of polymers has been studied for over 60 years [52]. Polyacetylene was the first electrically conducting polymer discovered in 1977 [53], other conducting polymers such as polypyrrole (PPy), polythiophene (PT) and polyaniline (PANI) have been developed over the last 30 years [52,54]. These materials typically exhibit electrical and optical properties that are comparable to metals and semiconductors, while retaining some of the advantages of conventional polymers [54]. Although the very first papers on conducting polymers were published more than 30 years ago, the importance and interest in these materials are constantly growing [55,56]. Polypyrrole (PPy), polyaniline (PANI), and poly(3,4-ethylenedioxythiophene) (PEDOT) are examples of conjugated polymers of which PANI is the most studied one and is used in the thesis [57,58].

4.1 Polyaniline

Polyaniline is a homopolymer with a *p*-linked phenylene amine imine structure (Fig. 2) characterized by easy synthesis and high environmental stability [59–61]. Depending on the degree of oxidation, PANI can exist in the form of salt or base. The oxidation states are given by a combination of benzenoid (amine N) and quinoid (imine N) rings. Three oxidation forms of PANI include leucoemeraldine (fully reduced, emeraldine (partially oxidized), and perningraniline (fully oxidized form), of which the emeraldine salt is the only conducting form of PANI [62–64]. Green emeraldine salt is an essential stable form of polyaniline with a typical conductivity in the range of 10^{-1}–10^{1} S cm^{-1}, which is usually formed by oxidation aniline, for example in the form of the hydrochloride or sulfate. Treatment of the protonated emeraldine salt with alkali produces a blue non-conducting emeraldine base with conductivity 10^{-10}–10^{-8} S cm^{-1}. Oxidation of emeraldine gives protonated blue pernigraniline, whose base is violet. Alternatively, by reduction of emeraldine, colorless, non-conducting leucoemeraldine can be obtained [65].



PANI

Figure 2 Chemical structure of polyaniline (PANI).

5. CONDUCTING COLLOIDAL DISPERSIONS

The concept of the preparation of colloidal particles relies on the presence of a stabilizer, for example, a polymer, in the reaction mixture [66]. First, the adsorption of the aniline oligomer on the stabilizer chains occurs followed by stimulation of chain growth and nucleus formation. Then other oligomers and new chains are formed near the nucleus and a colloidal particle grows. The diameters of the colloidal particles usually range from 200 to 400 nm [66,67]. The particles can be uniform in size or polydisperse with different morphologies from spheres to extended objects with a high aspect ratio [68]. Colloidal PANI has been studied by many researchers and research groups. Currently, the PANI colloids were prepared in the presence of various types of stabilizers that control their future application. For example, Gonçalves et al. prepared colloidal PANI-GA (gum Arabic) dispersions with excellent biocompatibility suitable for biological and biomedical applications. Thanks to easy synthesis and the sustainability of GA, this nanocomposite is promising for the development of clinically safe devices, thus expanding the possible applications of the composite [69]. In another study, Bober et al. prepared PANI–silver colloids stabilized by gelatine for application in regenerative medicine or biosensing [70].

Another interesting group of substances that can be advantageously used to stabilize conducting colloidal dispersions are biopolymers. Cellulose derivatives, such as ethyl(hydroxyethyl)cellulose (EHEC) [71] and hydroxypropylcellulose (HPC) [72], protein albumin [73] and gelatin [70] have been used for the synthesis of colloidal PANI. Recently, Kašpárková et al. (2019) prepared PANI colloids using biocompatible polysaccharides, sodium hyaluronate (SH), and chitosan as stabilizers. Both polysaccharides improved biocompatibility of CPs and can be used to stabilize conducting colloids, especially for biological applications [74]. The benefit of using biopolymer stabilizers for CPs lies not only in improving the processability of the resulting conducting composite but also in providing biocompatibility for potential biomedical applications [75].

5.1 Synthesis of conducting colloids

Dispersion polymerization is one of the possibilities to prepare a colloidal form of CPs. PANI and PPy are commonly synthesized by oxidative polymerization of their monomers (i.e. aniline and pyrrole) in an aqueous acidic medium in the presence of oxidizing agent (most frequently ammonium persulfate (APS) for PANI, and ferric chloride ($FeCl_3$) for PPy) and steric stabilizer [65]. The preparation of colloidal PANI according to the protocol of IUPAC in the presence of PVP as a stabilizer consists in dissolving 259 mg of aniline hydrochloride (AH) in 5 ml of an aqueous solution of PVP (40 g l^{-1}). The addition of 5 mL of an aqueous solution containing 571 mg of APS under brief stirring starts the polymerization, which is carried out at room temperature close to 20 °C. The reaction is completed within a few minutes [76]. In the case of PANI, the mixture

gradually turns blue, indicating the formation of a protonated, pernigraniline, which at the end of the polymerization changes to the final, protonated green emeraldine salt [65]. The principles leading to the formation of PANI or PPy are analogous and consist of the spontaneous attachment of oligomers formed *via* the oxidation of monomers in an acidic medium to a stabilizer, creating thus a nucleus for the PANI (or PPy) growth [65,77]. The dispersion polymerization method is characterized by typical features: a) the monomer is miscible with the reaction medium (as opposed to emulsion or suspension polymerization); b) the polymer formed during the polymerization is insoluble under the same conditions; and c) the macroscopic precipitation of the polymer is prevented by the presence of a stabilizer. Compared to monomers, such as styrene or methyl methacrylate, PANI and PPy are not soluble in their respective monomers and the polymerization can take place in the aqueous phase [65].

6. CONDUCTING THIN FILMS

Thin films are layers of material formed on a solid support (substrate) either directly by a physical process or *via* a chemical and/or electrochemical reaction [78]. In connection with CPs, it is an alternative strategy for their processing [76]. Stable conducting thin films are interesting research subjects and are widely used in many applications including optics, sensors, biomedical devices, etc. [79].

6.1 Synthesis of thin films

Thin films of PANI can be prepared chemically or electrochemically [80]. Electrochemical polymerization allows to control of the area and thickness of the resulting film [81]; however, this method requires the use of a conducting surface [82] and the resulting films are thinner compared to films prepared by chemical oxidation [83]. Chemical polymerization, therefore, represents a more general approach to the preparation of thin films [67].

The chemical method includes oxidative chemical polymerization of aniline in an acidic aqueous medium as a dopant and ammonium persulfate (APS) as an oxidizing agent [84]. Essentially any substrate present in the reaction mixture can be coated with a PANI film of submicrometre thickness [76]. The PANI film formation mechanism involves three steps: 1) adsorption of aniline oligomers at the interface (oligomers are more hydrophobic than the aniline cations and tend to separate from the aqueous medium, for example by adsorption on available surfaces), 2) stimulation of chain growth by oligomers and nucleus formation (the first surface-anchored PANI chain forms a nucleus of the future film), and 3) growth of other chains due to the auto-acceleration mechanism close to the nucleus. The chains then extend along the surface and, are preferably oriented perpendicularly for steric reasons (Fig. 3A) [66], resulting in a brush-like structure [67]. Depending on the reaction conditions, the film thickness varies from 100 to 400 nm. Many surfaces including polystyrene Petri dishes, glass, or metals can be

used as substrates for coating with a conducting thin film. The selection of a suitable surface plays an important role in the formation of a PANI film. The films are more uniform on hydrophobic surfacaes, whereas on hydrophilic substrates they have a globular structure [67]. Moreover, it was reported that the conductivity of films prepared on hydrophobic substrates might be higher compared to films prepared on hydrophilic substrate such as glass [85], which is explained by the different organization of PANI chains [86,87].

Besides standard chemical polymerization, dispersion polymerization can be used to prepare thin PANI films. This procedure involves adding a suitable steric stabilizer to the commonly used reaction mixture that contains aniline (aniline hydrochloride) and an oxidant [65,88]. The presence of a stabilizer that prevents macroscopic precipitation of the PANI results in a different morphology of the films and their surface roughness is significantly reduced [89]. The principles of film formation by dispersion polymerization are similar to formation of colloidal particles [88]. Dispersion films are thinner than PANI films prepared without stabilizer, which is due to the absence of PANI precipitate [89]. The organization of PANI chains on the film surface is also different and the chains do not show a brush structure, but lie loosely twisted on the substrate (Fig. 3B) [89].

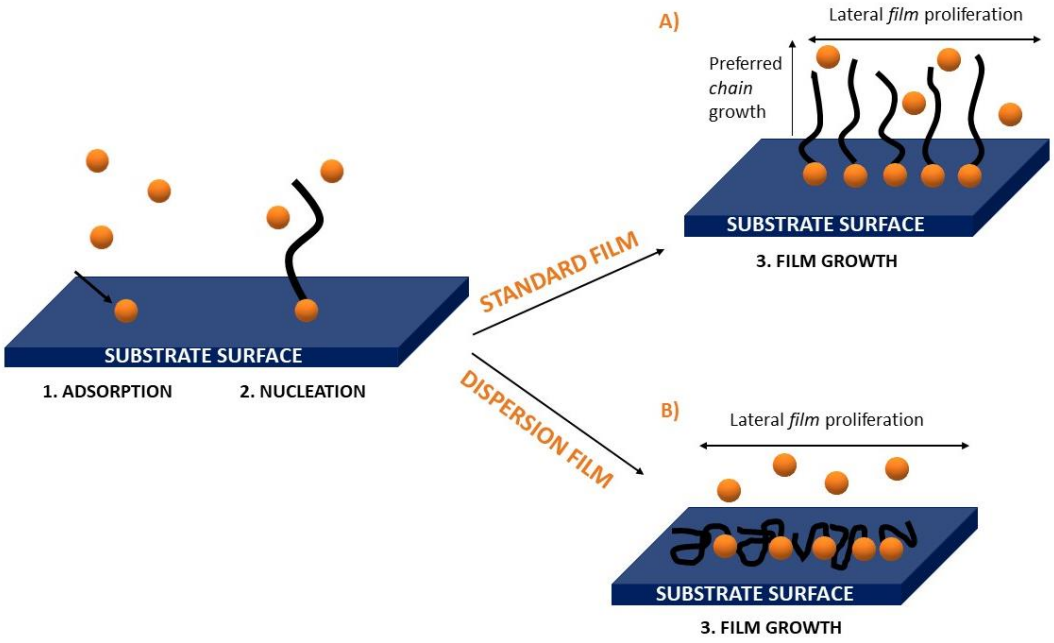


Figure 3 The model of PANI film formation.

7. AIMS OF WORK

The primary aim of the thesis is to increase knowledge about dispersion systems stabilized with solid particles, specifically cellulose (nano)particles. The particles are either combined with TiO_2 to form Pickering emulsions or utilized as a stabilizer for conducting PANI/cellulose composite colloids. The effort focuses on investigating and understanding the characteristics and behaviour of these classical and conducting dispersion systems. Particular emphasis is put on the formulation, production, and characterization of these systems, as well as the investigation of their biological properties. Intended applications of prepared colloidal systems are in the fields of biomaterials and cosmetics. The main goals of the work have been divided into following areas:

- The formulation of Pickering emulsions for skin photoprotection that are stabilized by a combination of **cellulose nanoparticles** and TiO_2, and the identification of a reliable and repeatable process for producing the emulsions at a lab scale.
    - A comprehensive examination of TiO_2 particle properties and behaviour under simulated *in vivo* and *in vitro* conditions. The information obtained here is critical for the successful integration of TiO_2 in the stabilizer layer of Pickering emulsions.
- Research into the ability of different types of **cellulose nanoparticles** to stabilize PANI in aqueous dispersion, with the goal of synthesizing PANI/cellulose ocomposite particles that can serve as 1) stabilizers of oil-in-water Pickering emulsions and 2) precursors for composite conducting films for potential biomedical applications.

8. EXPERIMENTAL

For clarity, the sections Experimental part, Result and discussion together with Summary of individual goals of the thesis are divided as follows:

a) **Study on cCNC/TiO_2-stabilized Pickering emulsions:** the follow-up study focused on the preparation of Pickering oil-in-water emulsions stabilized with pH-responsive carboxylated cellulose nanoparticles (cCNC) in combination with TiO_2 (a mixture of Rutile/Anatase). More specifically, the effect of formulation (ratio between cCNC and TiO_2) and preparation method (the Layer by Layer method *vs.* the conventional emulsification method) on the properties of final emulsions was studied. The emulsions could serve as platforms for skin photoprotection.

b) **Study on conducting colloidal systems:** the aim of the study was to develop three different types of conducting systems based on cellulose naoparticles – nanocrystals and nanofibers (CNC, CNF) and polyaniline (PANI). First and foremost, the study focused on the synthesis and characterization of PANI colloidal particles prepared by oxidative polymerization of aniline hydrochloride in the presence of CNC or CNF. The goal was to find a suitable composition of the reaction mixture that would results in stable colloids with favorable physico-chemical and biological properties. The colloids were then used to create other conducting systems for biological application, namely Pickering emulsions and thin films. The effect of the preparation process and formulation on the behaviour and properties of these systems was studied. In addition to physicochemical characterization, biological studies were also conducted.

8.1 Materials and methods

Ammonium peroxydisulfate (APS; 98 %), aniline hydrochloride (AH; reagent-grade ≥ 98 %), undecane, hydrochloric acid (HCl; 37 %), ethylene glycol, and diiodomethane were acquired from Sigma Aldrich (Germany). Cellulose nanocrystals (CNC; 12.2 wt% in water) and cellulose nanofibers (CNF; 3 wt% in water) were purchased from Cellulose Lab (Canada). Caprylic/capric triglyceride (T) was acquired from AceTrade (Czech Republic). Carboxylated cellulose nanocrystals (cCNC; 2.2 %) were prepared by oxidation of commercially available microcrystalline cellulose (Avicel PH101) with ammonium peroxydisulfate (APS; 98 %) (both supplied by Sigma Aldrich. A mixture of Rutile/Anatase (Cat No. 634662-25G) was purchased from Sigma Aldrich (Taufkirchen, Germany). Sodium chloride (NaCl) and calcium chloride ($CaCl_2$) were acquired from Ing. Petr Lukeš (Czech Republic).

Study on cCNC/TiO_2-stabilized Pickering emulsions

The oil-in-water (O/W) Pickering emulsions were prepared using tricaprylin/tricaprine (T) oil (dispersed phase), water (continuous phase), and a stabilizer made of carboxylated nanocrystalline cellulose particles (cCNC) and titanium dioxide (TiO_2, a mixture of Rutile/Anatase). Emulsions were prepared using two different methods. Specifically, the layer-by-layer (LbL) method and the conventional emulsification (CE) were used (Fig. 4). Pickering emulsions were created using sonication (UP400S sonicator, Heielscher, Teltow, Germany) in both cases. Regardless the preparation method, the sonication parameters remained unchanged, namely an amplitude of 30 % and a cycle of 0.6. Composition of emulsions is given in Tab. 2. The experiments also involved the preparation of emulsions containing electrolytes (in addition to all above mentioned ingredients). Specifically, NaCl (27 mmol L^{-1} in the aqueous phase) or $CaCl_2$ (3 mmol L^{-1} in the aqueous phase) were added.

Table 2 Composition of Pickering emulsions.

O/W ratio	Total stabilizer content [%]	cCNC:TiO_2 ratio	
20/80	0.5	3:2	4:1
30/70			
20/80	0.7	3:2	4:1
30/70			

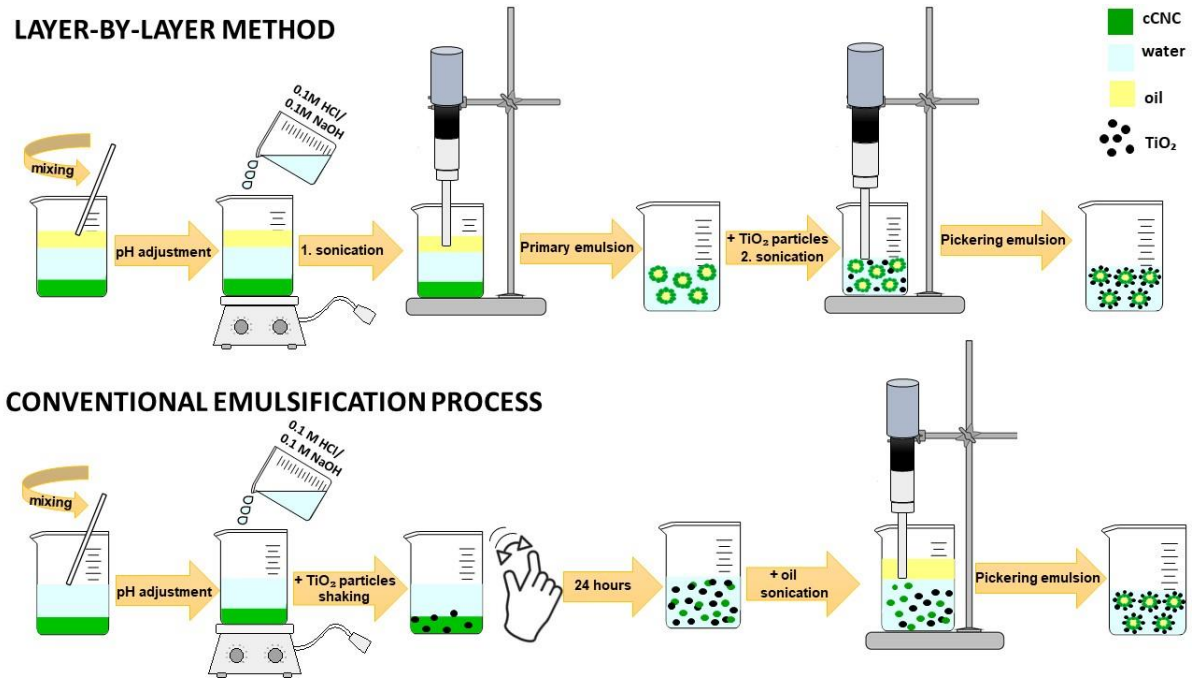


Figure 4 Schematic illustration of the formation of O/W Pickering emulsion.

Emulsions were characterized using laser diffraction (LD), zeta potential, phase studies and atomic force microscopy (AFM).

Study on PANI/cellulose colloidal dispersions and Pickering emulsions

A pre-formulation study was carried out to find the optimal composition of stable colloidal dispersions. A series of samples with varying amounts of CNC or CNF particles and reactants were prepared and the samples with the best stability, PANI/CNC and PANI/CNF (Tab. 3) were then used in subsequent experiments.

The synthesis was carried out by the oxidation of aniline hydrochloride (AH) with ammonium persulfate (APS) in the presence of each type of cellulose nanoparticles. For PANI/CNF, aqueous CNF dispersion was kept at 55 °C overnight and sonicated for 10 min at 60% amplitude using a UP400S sonicator (Hielscher, Germany) before being used. The polymerization then proceeded in the same way for both types of dispersions. Specifically, AH was dissolved in 5 mL of aqueous CNC or CNF dispersion and the polymerization was started at room temperature by adding 5 mL of aqueous APS solution to the reaction mixture. The polymerization was completed within 1 hour and the resulting colloidal dispersions were dialysed against 0.2M hydrochloric acid for 14 days.

Table 3 Compositions of the reaction mixtures of colloidal dispersions.

Nanocellulose type	Sample	CNC/CNF [wt.%]	AH [M]	APS [M]
CNC	PANI/CNC	1.0	0.2	0.05
CNF	PANI/CNF	0.06	0.2	0.2

PANI/CNC and PANI/CNF particles in colloidal dispersions were used as Pickering stabilizers to prepare oil in water (O/W) emulsions with 20 % oil phase composed either of undecane (U) or caprylic/capric triglyceride (T) (Tab. 4). To 8 g of colloidal PANI/CNC dispersion, 2 g of oil was added to form a Pickering emulsion. The sample was homogenized with UP400S sonicator (Hielscher, Germany) for 1 min at 30% amplitude on an ice bath. The preparation of Pickering emulsion with PANI/CNF proceeded in a slightly different way. At first, the PANI/CNF dispersion was diluted to either 30 or 50 % of initial concentration with demineralized water and then sonicated for 1 min at 30% amplitude. Then 2 g of oil were added to 8 g diluted PANI/CNF and the sample was sonicated again under the same conditions. A different approach based on dilution of CNF-based Pickering emulsions was used due to the mentioned poor dispersibility of CNF.

Table 4 Composition of Pickering emulsions (E) with O/W 20/80; oil phase: caprylic/capric triglyceride (T) or undecane (U); stabilized with PANI/CNC colloidal dispersion (non-diluted) or PANI/CNF diluted to 30 or 50 % of initial dispersion concentration.

Sample	**Stabilizer type**	**Dilution [%][a)]**	**Oil phase**
E-PANI/CNC^{T}	PANI/CNC	None	Caprylic/capric triglyceride (T)
E-PANI/CNF^{T30}	PANI/CNF	30	
E-PANI/CNF^{T50}	PANI/CNF	50	
E-PANI/CNC^{U}	PANI/CNC	None	Undecane (U)
E-PANI/CNF^{U30}	PANI/CNF	30	
E-PANI/CNF^{U50}	PANI/CNF	50	

[a)] Dilution relatively to initial 100% dispersion

Colloidal particles and Pickering emulsions were characterized by several analytical methods, such as dynamic light scattering (DLS), UV-vis spectroscopy, and transmission electron microscopy (TEM). The emulsion droplets were investigated by confocal laser scanning microscopy (CLSM). Biological properties were determined by testing of cytotoxicity, antioxidant activity, oxidative burst (ROS production), and nitric oxide (NO) and interleukin 6 (IL-6) production. Biological assays were performed on the murine peritoneal macrophage and isolated neutrophils.

Thin Films

For the synthesis of PANI/CNC composite films (Fig. 5), APS (0.05 mol L^{-1}) was dissolved in water and AH (0.2 mol L^{-1}) was dissolved in an aqueous solution of CNC (1 wt%). Similarly, for the synthesis of PANI/CNF films, APS

(0.2 mol L^{-1}) was dissolved in water and AH (0.2 mol L^{-1}) was dissolved in an aqueous solution of CNF (0.06 wt%). A solution of stabilizing CNF (0.06 wt%) was prepared by the CNF overnight dissolution in stirred demineralized water at 55 °C followed by sonication for 10 min at 60% amplitude. The polymerization was then started by mixing the AH/CNC or AH/CNF solution and APS at room temperature. The polymerization of PANI/CNF, the composite film was completed in 1 h. Because the first layer of PANI/CNC film was too thin, the procedure was repeated and a second layer of the film was deposited on the top of the first layer. The polymerization of each layer was completed in 24 h. The resulting composite films were rinsed with 0.2M hydrochloric acid, followed by methanol, and allowed to dry in air. As a reference, standard PANI films were prepared and synthesized in a similar manner without the use a stabilizer.

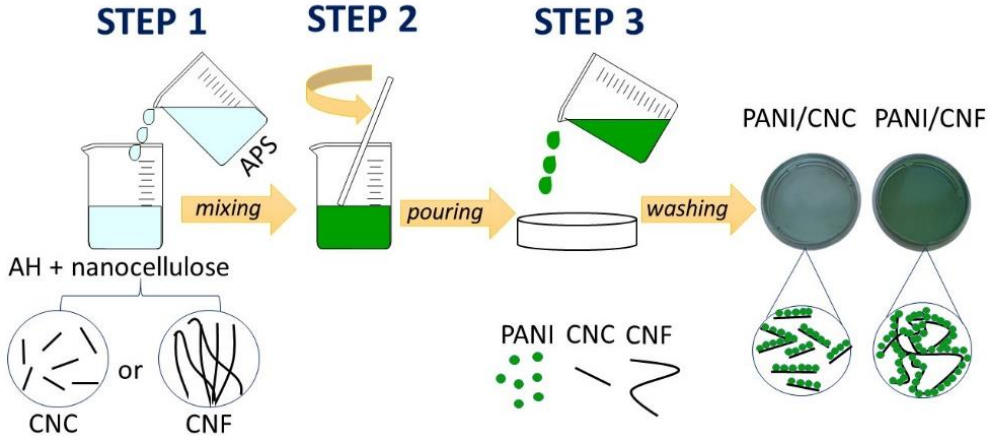


Figure 5 Schematic illustration of the synthesis of conducting thin films.

Physico-chemical properties of thin films were analysed by atomic force microscopy (AFM) and determination of surface energy and conductivity. Biological properties including cell proliferation assay and antioxidant as well as antibacterial activity were determined.

8.2 Results and discussion

The presented doctoral thesis is focused on the preparation of dispersion systems stabilized with solid particles, especially cellulose nanocrystals (CNC) and cellulose nanofibers (CNF). The understanding of the characteristics and behaviour of these classical and conducting dispersion systems with regard to their use in in the fields of biomaterials and cosmetics.

8.2.1 cCNC/TiO_2-stabilized emulsions

The goal of the second study was to develop a surfactant-free emulsions stabilized with nanocrystals of pH-responsive carboxylated cellulose (cCNC) in combination with TiO_2 particles (a mixture of Rutile/Anatase), which could provide an effective and safe alternative to conventional emlsions with sunscreen properties. Concerning the emulsion properties, the influence of preparation

procedure and compositions (a type of oil, O/W ratio, concentration of cCNC, TiO_2) must be taken into account. Here, knowledge gathered within thorough investigation of TiO_2 particles (Study on TiO_2 particles) were utilized to formulate Pickering emulsions with caprylic/capric triglyceride as oil. The most important findings are discussed below briefly.

- **Emulsions prepared at pH 3**

Layer-by-layer method. The utilization of the opposite charge of cCNC and TiO_2 particles at a given pH value, which induces complex formation between the two types of particles, was the principle of the successful stabilization of emulsions with layer-by-layer (LbL) method. This occurs for cCNC and TiO_2 at low pH (2 – 4.5). Therefore, emulsions at pH 3 were first prepared. Effect of the total content of stabilizers on average droplet size and zeta potential of the emulsions is given in Fig. 6 and 7. From the figures it is seen that correlation between stabilizer amount and droplet size was not unambiguous (Fig. 6) and depended on several variables. Emulsions with an O/W ratio of 20/80 prepared with 0.5 and 0.7 % stabilizer and cCNC:TiO_2 4:1 proved that the higher cCNC content in mixture led to smaller droplets compared to emulsions with a cCNC:TiO_2 ratio of 3:2. However, at O/W 30/70 this trend was not preserved.

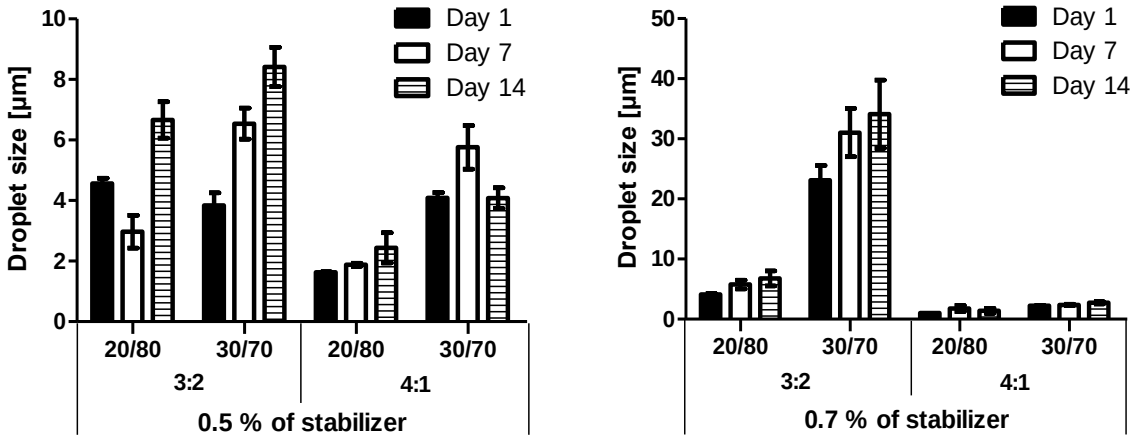


Figure 6 Size of emulsion droplets D[4,3]; dependence on the total stabilizer content (0.5; 0.7), cCNC:TiO_2 ratio (3:2, 4:1), and O/W ratio (20/80, 30/70).

Zeta potential measurements of the emulsions are given in Fig. 7. On the day of preparation, emulsions with 0.5 % stabilizer, an O/W ratio 30/70 showed a more negative zeta potential at both cCNC:TiO_2 ratios than 20/80 emulsions. However, this effect was not observed with emulsions containing 0.7 % of stabilizer.

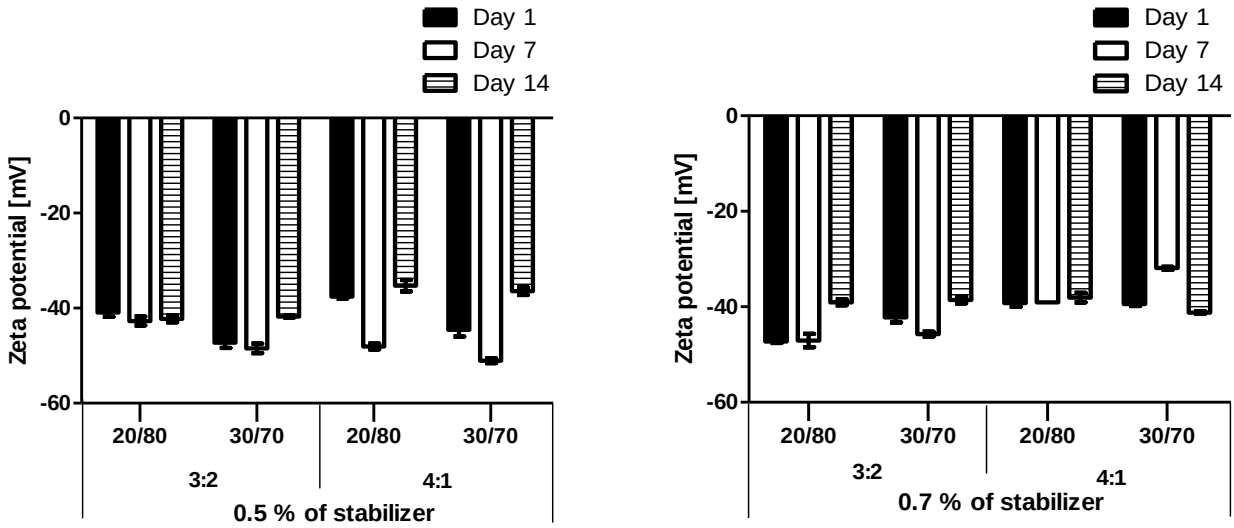


Figure 7 Zeta potential of emulsions; dependence on the total stabilizer content (0.5; 0.7), cCNC:TiO_2 ratio (3:2, 4:1), and O/W ratio (20/80, 30/70).

Conventional emulsification. With the attempt to determine whether another emulsification method could be used for the preparation of emulsions and how the method affected the properties of emulsions, the conventional emulsification (CE) method was chosen and compared with LbL method.

Measurement of the emulsion droplet size showed that, when compared to the LbL method, the CE method produced larger droplets regardless of O/W and cCNC:TiO_2 ratio (Fig. 8), which was likely due to the shorter sonication time used for their preparing. Interestingly, regardless of the preparation method used, the ratio of cCNC:TiO_2 of 4:1 resulted in smaller emulsion droplets compared to samples prepared with the 3:2 ratio at both studied O/W ratios of 20/80 and 30/70. The study of the effect of emulsification method on the zeta potential did not find any significant differences between the CE and LbL methods.

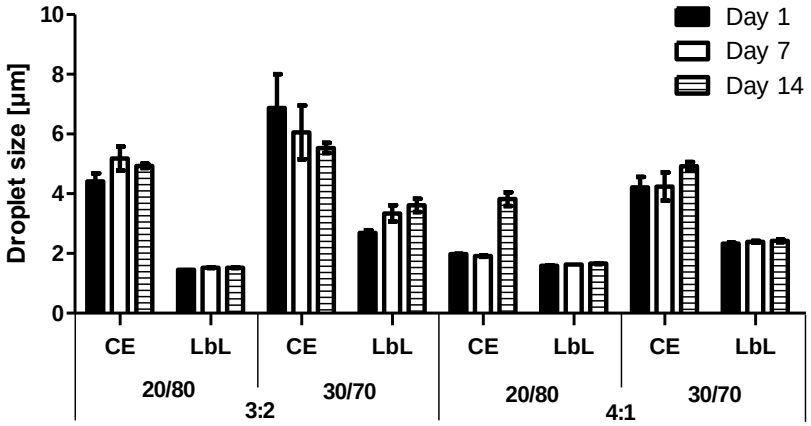


Figure 8 Size of emulsion droplets D[4,3]; dependence on the preparation method (CE, LbL), cCNC:TiO_2 ratio (3:2, 4:1), and O/W ratio (20/80, 30/70).

The conventional emulsification was shown to be effective for the preparation of emulsions stabilized by combinations of cCNC and TiO_2 particles at pH 3, with the encapsulation efficiency of all emulsions prepared by this method being 100 % for over a two-week period.

- **Emulsions prepared at pH 5**

In the following study, emulsions were produced at pH 5, which is more appropriate for topical applications. However, cCNC and TiO_2 particles did not normally form complexes at this pH. Nevertheless, studies [90,91] suggest that adding inorganic salts to cCNC-containing emulsions can promote complex formation. As a result, the effect of added NaCl ($CaCl_2$) on emulsion formation was investigated. At this pH, emulsions were succesfuly prepared by both LbL and CE. Results of the experiment showed that LbL method led to the formation of relatively stable emulsions in the presence of both NaCl and $CaCl_2$ used. Using CE, it was possible to prepare emulsion only in presence of $CaCl_2$.

As regards influence of electrolytes, their addition increased droplet size regardless of the preparation method and type of salt. Moreover, irrespective of the preparation method or electrolyte used, an O/W ratio of 30/70 always produced larger droplets than O/W 20/80 (Fig. 9). The preparation method had a considerable impact on the size of emulsion droplets. When employing the CE approach, bigger emulsions droplets were formed, likely due to the shorter sonication time or different mechanism of stabilization.

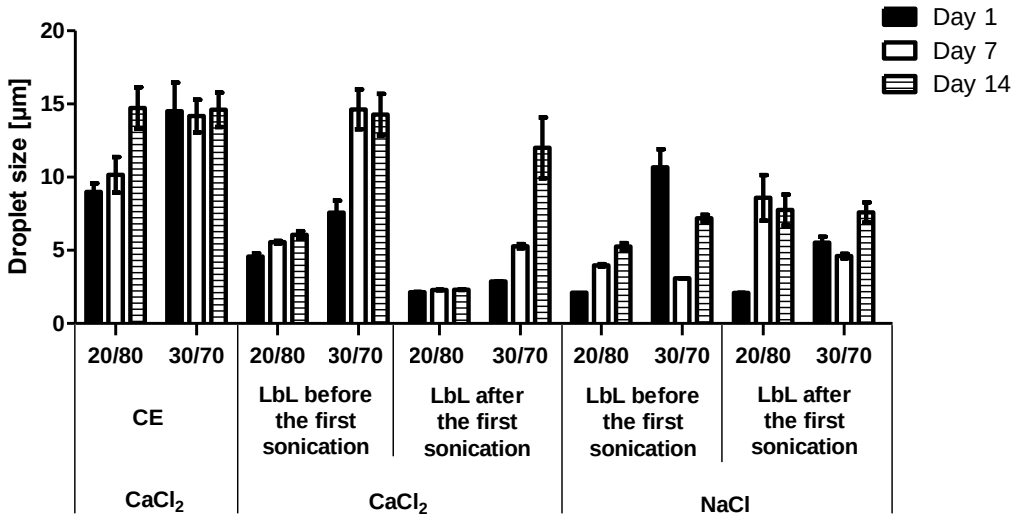


Figure 9 Size of emulsion droplets D[4,3]; dependence of preparation method (CE, LbL), O/W ratio (20/80 and 30/70) and the type of electrolyte used. Ratio cCNC:TiO_2 was 4:1.

Briefly summarised, the effect of different cCNC:TiO_2 and O/W ratios on emulsion properties revealed that with the increasing amount of cCNC in the emulsions, their stability improved. This suggests that cCNC particles were

primarily involved in the stabilization of the emulsions. The most stable and the most promising formulation for potential use in practice was an emulsion with the 0.5 % stabilizer, cCNC:TiO_2 ratio of 4:1 and the O/W ratio of 20/80. It was also demonstrated that, in addition to the layer by layer (LbL) method, the conventional emulsification (CE) method can be used for the preparation of stable emulsions under mentioned conditions at pH 3. The final goal of the study was to prepare emulsions at pH 5. The results confirmed that at pH 5, emulsions stabilized by cCNC and TiO_2 particles can be prepared only with the aid of electrolytes. The study thus resulted in the preparation of an effective and ecological emulsions with possible uses in UV protection.

8.2.2 Colloidal dispersions and Pickering emulsions

The aim of this study was to investigate whether stable, bioactive PE could be made of colloidal particles composed of conducting polymer PANI and biocompatible cellulose nanoparticles (CNC or CNF). PE bioactivity was assumed to be derived from these composite particles used for PE stabilization and the encapsulated oil. Therefore, the PANI/CNC (or PANI/CNF) particles were first prepared and characterized. The next step was to prepare PE from these particles and an oil phase of undecane or caprylic/capric triacylglyceride. Finally, extensive characterization of their biological properties were conducted, primarily focusing on antioxidant activity in terms of immune response studies and scavenging ROS. This work, therefore, fills a knowledge gap and adds novelty to the field of PE.

- **Colloidal particles**

The size distribution of PANI/CNC and PANI/CNF particles was measured by DLS. The data revealed that the studied samples had large particle sizes (Tab. 5) and larger particle size was surprisingly measured for PANI/CNC both before and after dialysis. Although the particles of the non-dialyzed PANI/CNF were also relatively big, their sizes decreased after dialysis and were of approximately half the size compared to dialysed PANI/CNC. This decrease in the size of PANI/CNF colloidal particles after dialysis could be attributed to size changes in CNF fibres under dialysis due to the removal of residual low-molecular weight salts and reactants. The larger particle sizes of nanocellulose-based PANI colloids, compared to other polysaccharide PANI colloids (hyaluronate or chitosan) [92], are due to their more complex morphology and the formation of clusters, in which the cellulose nanoparticles are interconnected PANI (Fig. 10).

Table 5 Z-average particle diameter (z-average ± SD) of PANI/CNC and PANI/CNF colloidal particles.

	Z-average [nm]	
	Before dialysis	**After dialysis**
PANI/CNC	2983 ± 43	3163 ± 26
PANI/CNF	2200 ± 33	1214 ± 18

Microscopic images of colloidal dispersions were captured using TEM (Fig. 10). Images confirmed that after polymerization, clusters of CNC particles interconnected by PANI chains formed, mainly in PANI/CNC colloidal particles (Fig. 10). In the PANI/CNF sample, spherical PANI particles covering the CNF fibers are visible (Fig. 10), whereas PANI/CNC displays mesh-like structure with CNC clusters interconnected with PANI. As a result, the fibrous morphology of CNF seems to offer a better substrate for the polymerization of polyaniline.

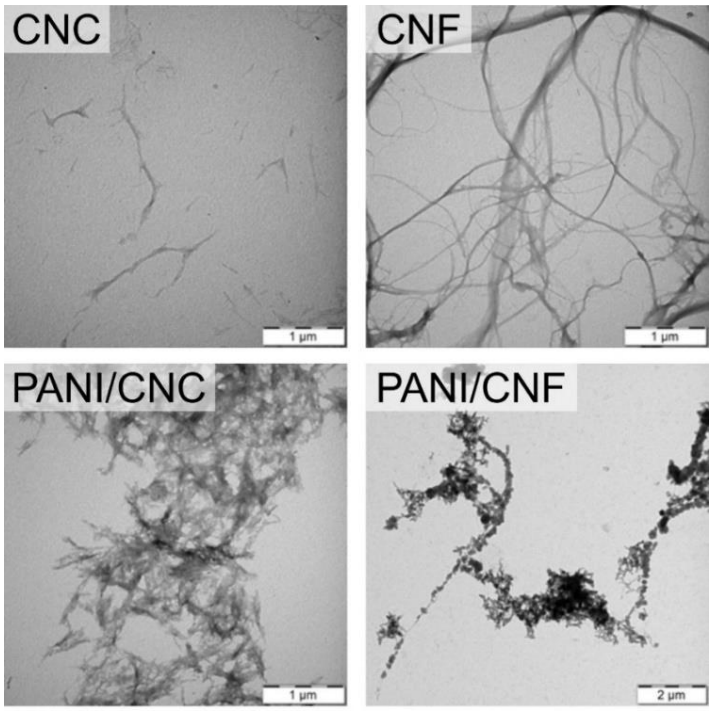


Figure 10 TEM images of CNC, CNF, PANI/CNC and PANI/CNF particles.

The presence of PANI polymer in particles was confirmed by UV-vis spectra (Fig. 11). The UV–vis absorption spectra of PANI/CNC and PANI/CNF showed typical maxima at λ ~361 and ~768 nm for PANI/CNC, and λ ~390 and ~794 nm for PANI/CNF. Stejskal and Sapurina [76] reported absorption maxima of colloidal PANI stabilized with poly(*N*-vinylpyrrolidone) at λ = 392 and λ = 854 nm, which slightly differ from the maxima of the here-tested samples. The first absorption band is assigned a π–π* transition of benzenoid ring, whereas the second absorption band belongs to the π–polaron and polaron–π transitions [67]. The above characteristics of PANI/CNC and PANI/CNF hence confirm the formation of PANI in the dispersions. The concentrations of PANI in colloids

were calculated using the procedure reported in [93]. Overall, a higher concentration of PANI was present in PANI/CNF (5762 μg mL^{-1}), compared to PANI/CNC (3676 μg mL^{-1}).

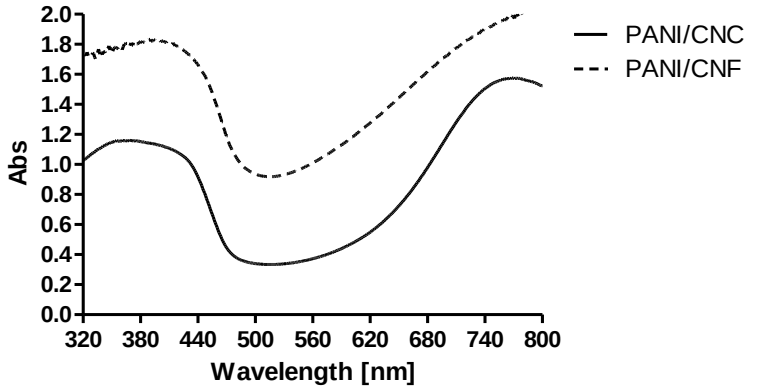


Figure 11 UV–vis spectra of PANI/CNC and PANI/CNF colloids.

In order to investigate the cytotoxic effect of colloidal dispersions, murine peritoneal macrophage RAW 264.7 cell lines were used. Cytotoxicity testing revealed that PANI/CNC had no cytotoxic effects on macrophages (Fig. 12) even at the lowest used 10% dilution, which corresponds to 368 μg PANI/mL. The increased viability of cells on PANI/CNC is due to interference of the absorbance of the released PANI into the culture medium. However, on the basis of microscopic observation, no morphological differences from untreated cells were observed. Thus, the PANI/CNC does not affect the viability of the used cells. On the other hand, PANI/CNF was not toxic at 1% dilution, but at 2.5% (144 μg PANI/mL) showed weak toxicity (viability of 66 %). The other dilutions corresponding to a PANI concentration higher than 288 μg PANI/mL were toxic (viability under 50 % compared to the reference) (Fig. 12).

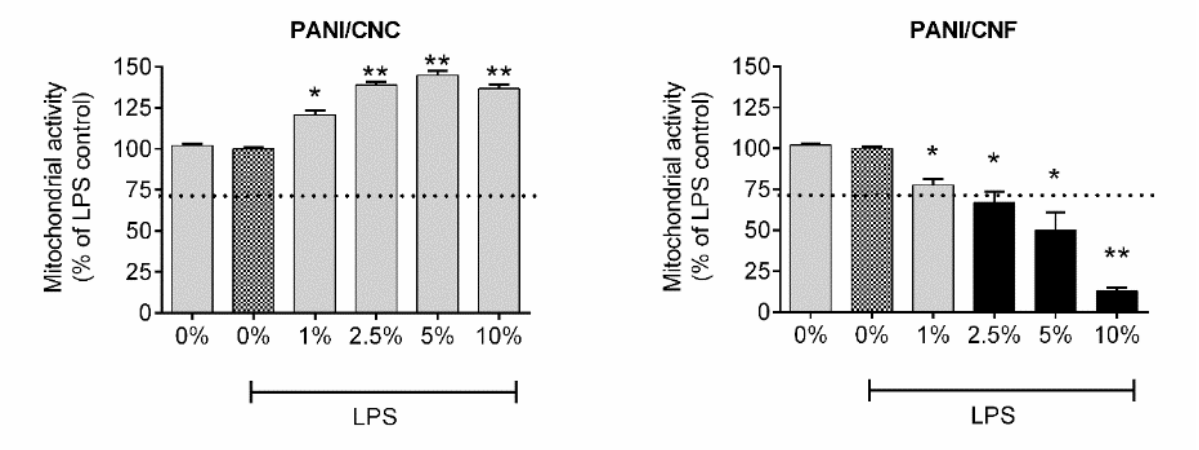


Figure 12 Cytotoxicity of PANI/CNC and PANI/CNF colloidal dispersions. Dashed line corresponds to cytotoxicity limit (70% viability relativelly to reference).

The antioxidant activity of a sample plays an important role in reducing immune response and the chemiluminescence signal. To exclude the direct scavenging effects of the colloidal dispersions, their antioxidant properties were measured in a luminol-HRP-H_2O_2 cell-free system. Tests demonstated strong antioxidant activity of both PANI/CNC and PANI/CNF, which were both able to reduce the chemiluminescence signal below 5 % of the total signal produced by the system itself (Fig. 13).

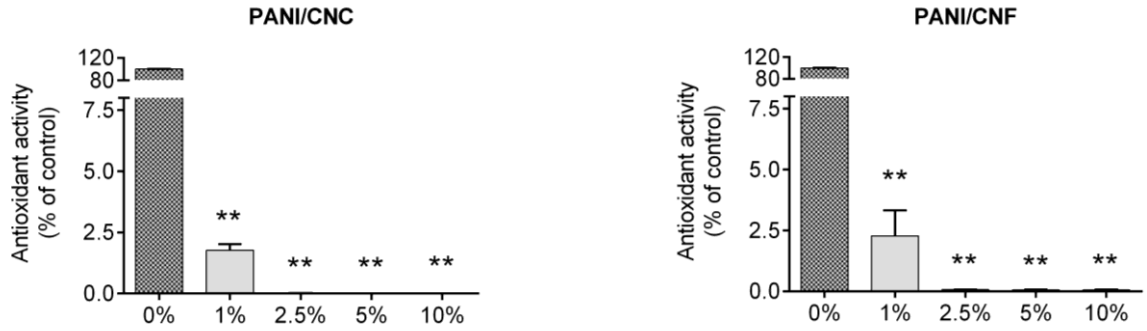


Figure 13 The antioxidant activity of colloidal dispersions.

In the next step, the effect of colloidal particles on the detectable amount of ROS produced by neutrophils spontaneously and after their activation was tested.

Data confirmed the ability of both PANI/CNC and PANI/CNF to strongly reduce ROS production in a concentration-dependent manner in both spontaneous and OZP-stimulated neutrophils. Given the antioxidant activity of the tested colloidal dispersions (Fig. 13), the reduction of ROS production is probably related to ROS scavenging activity.

The results also showed that the PANI-containing dispersion were able to inhibit growth of both gram positive and gram negative bacteria. Despite having a lower concentration of PANI polymer (3676 μg/mL), PANI/CNC had higher activity against both strains than PANI/CNF with a PANI concentration of 5762 μg/mL. Here, it can be speculated that PANI polymer is more accesible for antibacterial action in PANI/CNC particles than in PANI/CNF, where it can be hidden in the entangled CNF fibres. PANI/CNC had a lower MIC value against gram negative *E. coli* (1.7 μg/mL PANI in dispersion) than against gram positive *S. aureus* (3.4 μg/mL PANI in dispersion), which was also observed for colloidal PANI particles stabilized with chitosan and sodium hyaluronate [92]. In the PANI/CNF sample, the effects against both strains were similar with MIC detected at a PANI concentration of 8.3 μg/mL. Given the low antibacterial activity of colloidal PANI containing poly(*N*-vinnylpyrrolidone) reported by [94], the incorporation of cellulose nanoparticles, whether CNC or CNF, significantly altered the antibacterial efficacy of the here-examined samples.

- **Pickering emulsions**

PANI/CNC or PANI/CNF particles were used to stabilize Pickering emulsions with 20 % undecane (U) or caprylic/capric triglyceride (T). The size of E-PANI/CNC^{T} droplets was 2985 ± 6 nm. Thus, there was only a minimum increase in the size of emulsion droplets in comparison with the PANI/CNC particles. This is likely caused by the effect of sonication, which destroys the mesh-like structure of the PANI/CNC particles used to stabilize emulsions, reducing their size and allowing them to form emulsion droplets. Emulsions stabilized with the same particle type containing undecane (E-PANI/CNC^{U}) revealed droplets larger than 3000 nm (3399 ± 51 nm). Because the emulsion droplets were too large for DLS measurements and unsuitable for measurements by laser diffraction (PANI in emulsions could cover the measuring cell of the instrument with a green film), the droplet sizes of emulsions stabilized with PANI/CNF were determined using microscopy combined with image analysis. Average size of E-PANI/CNF^{U} droplets was of 33 μm, with range from 6.5 to 81 μm, and E-PANI/CNF^{T} droplets were smaller, with an average size of 19 μm ranging from 4.7 to 30 μm.

All prepared Pickering emulsions demonstrated excellent encapsulation efficiency, with no evidence of oiling-off in the samples after storage at room temperature. However, creaming, a process caused by the different densities of the oil and water phases, was clearly demonstrated (Fig. 14). This figure also shows how the concentration of stabilizing particles affected creaming in PANI/CNF-based emulsions. Creaming was lower in emulsions stabilized with PANI/CNF at 50 % initial concentration than in emulsions prepared with dispersions diluted to 30 %. Nevertheless, all emulsions could easily be re-dispersed by soft shaking, showing that creaming in the studied emulsions did not indicate a loss of their stability [25]. However, dilution of the initial PANI/CNF dispersion was critical because emulsions prepared with undiluted dispersion were unstable. PANI/CNC-based emulsions were stable in terms of encapsulation efficiency and creaming even after two years of storage at room temperature.

Figure 14 Creaming of Pickering emulsions with undecane (U) and caprylic/capric triglyceride (T) oils stabilized with PANI/CNF: E-PANI/CNF^{T50}; E-PANI/CNF^{T30}; E-PANI/CNF^{U50}; E-PANI/CNF^{U30} after preparation.

The appearance and morphology of emulsion droplets were investigated using confocal laser scanning microscopy (CLSM), (Fig. 15). Undecane produced emulsions with larger droplets than caprylic/capric triglyceride oil, regardless of the type of PANI/cellulose stabilizer used. These variances may be due to differences in physicochemical properties of the oils, such as density, polarity, or viscosity. Furthermore, images of PANI/CNF-stabilized emulsions revealed the presence of residual CNF fibers adsorbed around the emulsion droplets, providing additional stabilization.

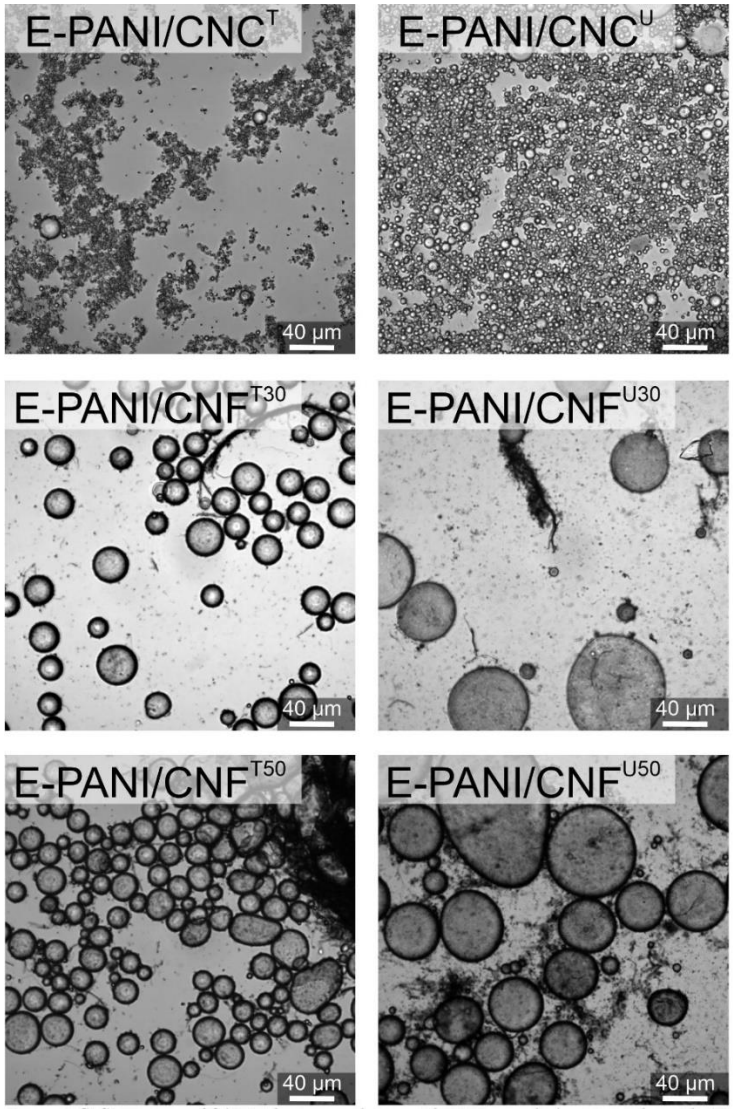


Figure 15 CLSM images of O/W Pickering emulsions with 20 % caprylic/capric triglyceride (T) and undecane (U).

As mentioned previously, PANI/CNC dispersions were not cytotoxic, whereas PANI/CNF showed toxicity at concentrations of dispersion higher than 2.5 % (Fig. 12). According to [95], undecane was among the major hydrocarbons associated with high cytotoxicity in human epidermal keratinocytes. Triglycerides, on the other hand, show very low levels of toxicity in laboratory

animals and humans after oral, parenteral or dermal administration [96]. These differences in oil cytotoxicities are reflected by the results presented in Fig. 16, revealing that triglyceride-based emulsions E-PANI/CNC^{T} had no cytotoxic effects on macrophages, whilst E-PANI/CNC^{U} with undecane showed strong cytotoxicity at all concentrations tested. The results also show that cytotoxicity was higher in undecane-containing emulsions stabilized with PANI/CNC than in emulsions stabilized with PANI/CNF. This could be due to the formation of a thicker, more impermeable PANI/CNF layer protecting the oil droplets from undecane leakage. Nevertheless, the cytotoxicity of PANI/CNF-stabilized emulsions with triclyceride was higher than that of PANI/CNC emulsions and was dependent on the sample concentration used for testing.

The cytotoxicity of the PANI/CNC dispersion (Fig. 12) and corresponding emulsions (Fig. 16) revealed that the triglyceride oil had no cytotoxic effects on macrophages, but undecane significantly reduced their viability, and the samples were cytotoxic at all tested concentrations. As a result, PANI/CNC colloids retained their properties when used as emulsion stabilizers. Similar conclusions can be drawn for PANI/CNF dispersions and their emulsions. Dispersions were cytotoxic at 2.5 % dilution (144 μg/mL PANI) and emulsions prepared with non-harmful triglyceride oil exhibited cytotoxicity at a dilution of 5% corresponding to 115 μg/mL PANI. However, emulsions with undecane prepared with the same concentration of PANI/CNF showed severe cytotoxicity with a cell viability of only 5 %.

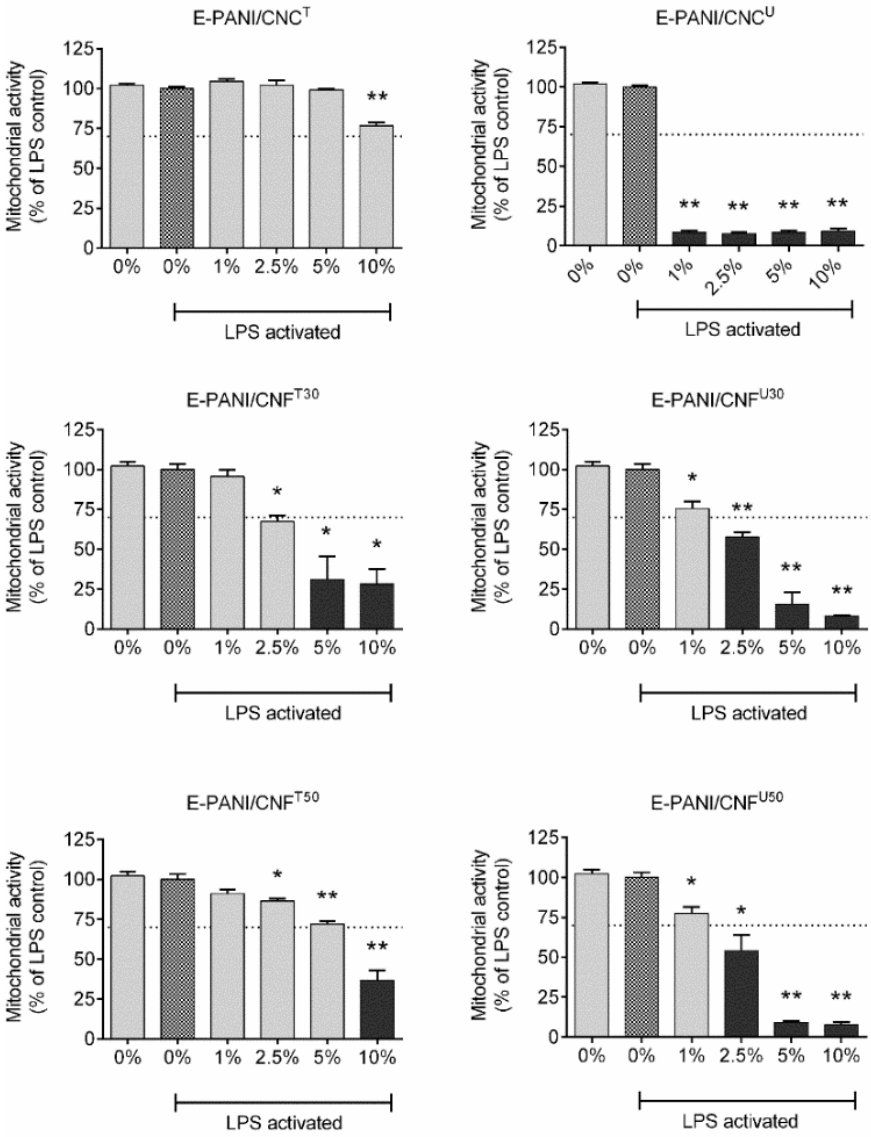


Figure 16 Cytotoxicity of Pickering emulsions expressed as cell viability of murine macrophage RAW 264.7 cells. Dashed line corresponds to cytotoxicity limit (70% viability relativelly to reference).

Correspondingly to the strong antioxidation activity of PANI/CNC dispersions, the results demonstrated the strong antioxidation activity of emulsions prepared with these particles – specifically, E-PANI/CNC^{T} and E-PANI/CNC^{U}. All tested concentrations were able to reduce the chemiluminescence signal to below 5 % of the total signal produced by the system itself. As regards PANI/CNF-based emulsions, at 1% dilution, E-PANI/CNF^{T50} and E-PANI/CNF^{U50} reduced the chemiluminescence signal to approximately 10 to 15 % of control. The other concentrations reduced the chemiluminescence signal to below 5% of control.

The thesis provides detailed information on additional biological testing, such as the impact of Pickering emulsions on neutrophil OZP-activated ROS generation as well as spontaneous ROS production and on the impact of Pickering emulsions on RAW264.7 macrophages' ability to produce NO.

In summary, the oxidative polymerization of aniline with ammonium persulfate in the presence of each of the mentioned cellulose particles resulted in composite particles (PANI/CNC and PANI/CNF) containing conducting polyaniline (PANI) and cellulose nanocrystals (CNC) or nanofibers (CNF). Testing of the biological properties of the particles provided information on their cytotoxicity and antioxidation activity, and demonstrated their immunomodulatory effect on macrophages. The detection of anti-inflammatory activity was crucial in this case. The study further revealed that PANI/CNC composite had better antibacterial activity against the two most common bacteria *S. aureus* and *E. coli*.

In the next step, Pickering emulsions containing 20 % undecane or an equal amount of capric/caprylic triglyceride oil were successfully formulated using PANI/CNC or PANI/CNF. The biological activity of the particles used to stabilize the emulsions was preserved in these systems, whereas the physico-chemical and biological properties of the emulsions were determined by the properties of the particles used for stabilization and the type of oil in emulsions.

In conclusion, these systems demonstrated strong antioxidant and ROS scavenging activity, indicating their potential use in biomedical applications, particularly wound healing.

8.2.3 Thin PANI/celulose films

The objective of this study was to investigate whether two different types of thin conducting composite films based on PANI and cellulose nanocrystals (CNC) or cellulose nanofibers (CNF) could serve as a suitable substrate for cells. The novelty of the study stems not only from a unique comparison of two types of nanocelluloses used in the preparation of composite films under the same conditions using *in situ* oxidative polymerization method, but also in the thorough physicochemical and biological characterization that contributes to a deeper understanding of cell behaviour on these surfaces.

When considering materials suitable for biomedical applications, the surface morphology of the material is an important characteristic influencing cellular behaviour. Therefore, the surface topography and surface electrical properties of the films were determined using AFM. The topography of the PANI/CNC and PANI/CNF films was significantly different compared to the pristine PANI (Fig. 17). The PANI film without cellulose nanoparticles showed a typical granular surface and a noticeably higher surface roughness ($Sa \sim 100$ nm). Despite having comparable thicknesses (21 and 25 nm), the two composite films showed different properties. The film of PANI/CNC exhibited rough structure with needle-like structures of celluloses visible on the surface. These structures are typical for cellulose nanocrystals, and the image thus confirms that the CNC was incorporated into the PANI composite film. Moreover, the structures are well connected to one another, which indicate the existence of strong hydrogen bonding [97]. On the other hand, the PANI/CNF film contained fibre aggregates

rather than the long nanofibers typical of CNFs without PANI. Regarding the electrical properties of the composites, the results from AFM showed that PANI/CNF exhibited considerably higher surface conductivity than PANI/CNC, which is in good agreement with the conductivities obtained with the van der Pauw method.

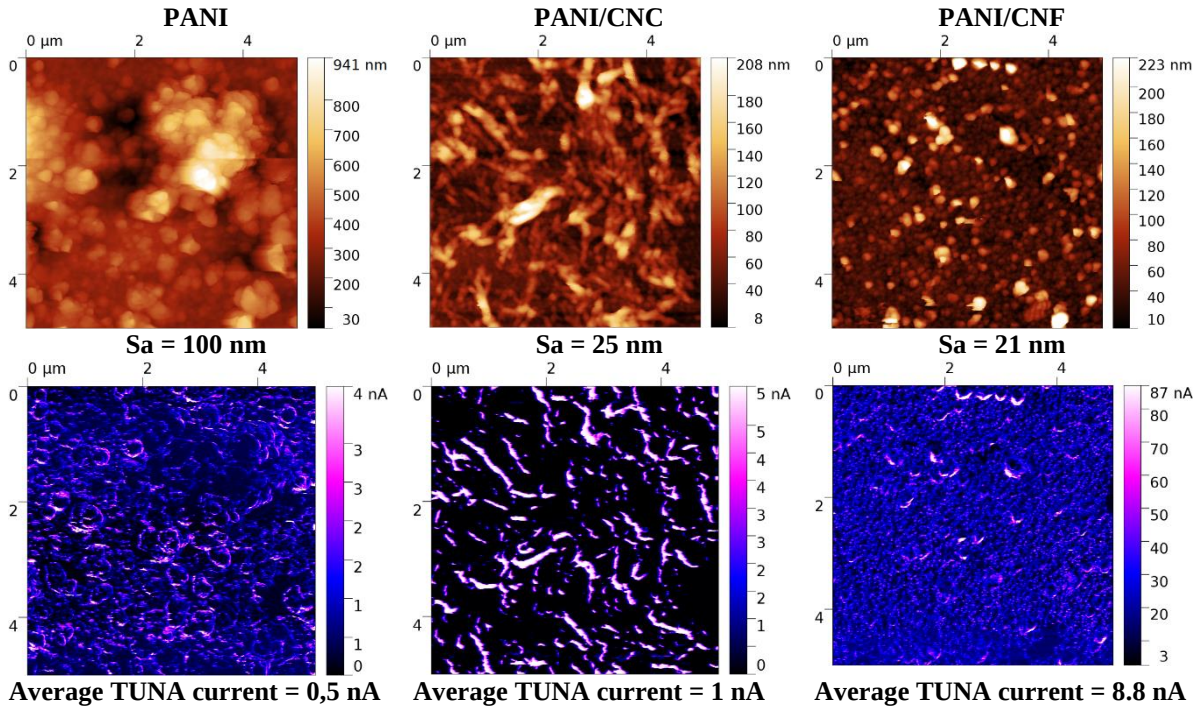


Figure 17 AFM images of PANI reference film and composite films of PANI/CNC and PANI/CNF. Top images show height changes, below TUNA current maps.

The measurement of surface energy revealed that the values of the total surface energy (γ^{tot}) of PANI/CNC corresponded to that of PANI film determined earlier [98] (Tab. 6). In addition, the PANI/CNC sample showed almost the same values of the surface energy components representing both disperse (γ^{LW}) and polar (γ^{AB}) parts as reference PANI without cellulose nanoparticles. This may indicate that the properties of PANI predominated and affected the surface characteristics of PANI/CNC composite film. Compared to these two samples, the total surface energy (γ^{tot}) and disperse (γ^{LW}) part of PANI/CNF were slightly higher. In contrast, polar (γ^{AB}) part of PANI/CNF was the lowest of all surfaces. Interestingly, surface energy values γ^{tot} obtained for the cell monolayer of NIH/3T3 cells [99] were close to the reported PANI/CNC and PANI/CNF values, which could indicate suitable biological properties of such surfaces.

Table 6 Contact angles together with total surface energy (γ^{tot}) and it's disperse (γ^{LW}) and polar (γ^{AB}) parts determined on tested PANI, PANI/CNC, and PANI/CNF surfaces.

Sample	Contact angles (°)			Free surface energy (mN m^{-1})		
	Water	Ethylene glycol	Diiodomethane	γ^{TOT}	γ^{LW}	γ^{AB}
PANI*	n.r.	n.r.	n.r.	52.5	46.1	6.5
PANI/CNC	51.3 ± 2.0	30.1 ± 0.9	20.5 ± 0.8	52.7	47.6	5.1
PANI/CNF	40.8 ± 1.2	9.5 ± 1.3	4.3 ± 3.0	54.8	50.7	4.2

* The values adopted from [98]; n.r. not reported

The conductivity is considered as important cell-instructive characteristic in biomedical applications. The virgin PANI films commonly show conductivity values within units of S cm^{-1} [76] depending on the conditions of polymer synthesis and dopant used. In here presented study, the conductivities of PANI/CNC and PANI/CNF composite films differed from each other with the higher PANI/CNF conductivity of 4.7 S cm^{-1}, close to of the virgin PANI film (5.5 ± 0.7 S cm^{-1}) [100]. In contrast, the PANI/CNC film displayed a significantly lower conductivity of 0.1 S cm^{-1}. Assuming almost identical thicknesses of PANI/CNC and PANI/CNF films determined by AFM (S_a values in Fig. 17), the differences in the conductivity of PANI/CNF and PANI/CNC films can be attributed mainly to the different morphology of the CNC and CNF particles. In comparison to small needle-like CNC, long CNF fibres can provide superior support for growth of conducting PANI. In addition, the concentrations of CNC (1 %) and CNF (0.06 %) used in the samples can explain this difference. Despite the presence of nanocellulose, the results demonstrated that the composite films retained good electrical conductivity.

The DPPH assay was used to determine the *in vitro* antioxidant activity of the films. The ability of polyaniline and its composites to act as antioxidants has previously been confirmed by published studies [101–104]. Also this work showed that PANI/CNC and PANI/CNF films are effective scavengers of DPPH radicals. Moreover, the analyses revealed that the activity of the samples did not differ significantly, with both samples demonstrating similar scavenging activity of about 50 % in 10 min.

The cell proliferation on tested surfaces is crucial for their use in biomedical materials. The results of cell proliferation on the composite films are presented in Fig. 18. The micrographs clearly show that the cells reached semi-confluence on the tissue polystyrene culture dishes used as a reference (Fig. 18a). Interestingly, the proliferation of NIH/3T3 cell line on the composite films was fully comparable to the reference (Fig. 18b, c), which indicates

properties favourable for cell growth. Also proliferation of cells on virgin PANI film reported in [99] was comparable to that on the tissue polystyrene culture dishes. Therefore, the presence of CNC or CNF in the composite films does not affect the cell proliferation, confirming absence of their *in vitro* cytotoxicity.

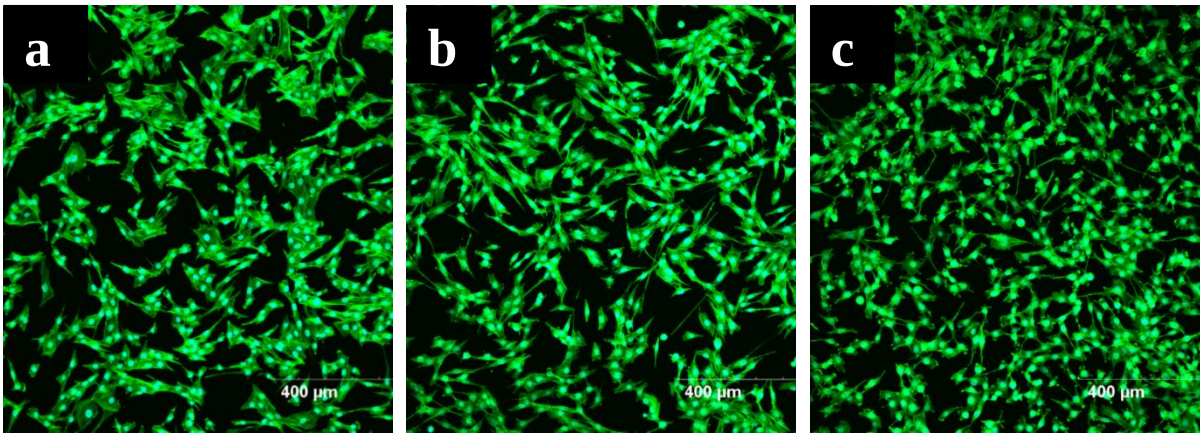


Figure 18 Proliferation of NIH/3T3 cells on studied films recorded after 48 h cultivation: a) Reference – tissue polystyrene culture dishes; b) PANI/CNC; c) PANI/CNF.

It is well known that nanocellulose itself has no antimicrobial properties [105]. To achieve antimicrobial activity, surface functionalization of nanocellulose with suitable antibacterial agent is required, which allows a wide application rage of such composites as an antimicrobial materials [106]. On the other hand, the antibacterial activity of PANI has already been demonstrated both in films [107] and colloidal particles [92]. It is therefore expected that the antibacterial effect of the composites will be caused primarily by PANI present in the composite film.

According to the protocol used for antibacterial testing, an antibacterial agent is considered effective if its antimicrobial activity R > 1. The antibacterial properties were assesed using EN ISO 20743:2021. The criteria for antibacterial efficacy (R) given at the standard are following: R < 2 corresponds to a low level of efficacy, 2< R <3 a significant level of efficacy, and R > 3 a strong level of efficacy. Results in Tab. 7 reveal that both PANI/CNC and PANI/CNF have low antibacterial activity against both gram positive *Staphylococcus aureus* and gram negative *Escherichia coli* bacterial strains. The results further demonstrate somewhat higher efficacy of both composites against *E. coli*.

Table 7 Number of viable bacteria N and antibacterial activity R of PANI/CNC and PANI/CNF composites.

Sample	**Antimicrobial activity *R***	
	S. aureus	*E. Coli*
PANI/CNC	1.26	1.30
PANI/CNF	1.26	1.30

In this study, electrically conducting nanocellulose-based polyaniline (PANI) composite films were prepared by *in-situ* oxidative polymerization of aniline hydrochloride in aqueous nanocellulose suspension (CNC or CNF) by using APS as oxidant. The PANI/CNC and PANI/CNF composite films displayed good conductivity, which was higher for the PANI/CNF (4.7 S cm^{-1}). The surface topography of the films was controlled by the type of cellulose nanoparticles present in the sample, and the thicknesses of both films were comparable. The surface energy values were not significantly different and were similar to the surface energy od cell monolayer of NIH/3T3 cells, indicating that both films had favourable biological properties. The composites also demonstrated *in vitro* antioxidation activity as determined *via* scavenging of DPPH radicals and mild antibacterial efficiency against gram positive *Staphylococcus aureus* and gramnegative *Escherichia coli.* Biological testing demonstrated that both PANI/CNC and PANI/CNF have exellent cytocompatibility, comparable to tissue polystyren. The presence of cellulose in the films have no effect on cell proliferation. As a result, the biocompatible nanocellulose-based composites formed may be promising materials for use in biomedicine.

9. CONTRIBUTION TO SCIENCE AND PRACTICE

The stability of colloidal systems is a fundamental prerequisite for their use. In this context, one of the key areas of colloid research is the development of new colloid stabilizers. The increasing application of renewable, biodegradable, green materials, which is in the focus of this thesis, has attracted global interest in the drive towards sustainable development. As a result, the thesis deals with the particle-based stabilizers obtained from celluose (CNC and CNF) and their ability to stabilize different types of dispersions and systems derived from them. The most important contributions of the doctoral thesis to science and practice are outlined in the following points:

A novel eco-friendly system for UV protection with potential applications in cosmetic practice has been created. Surfactant-free emulsions with anticipated sunscreen properties were prepared by combining pH-responsive carboxylated cellulose nanocrystals (cCNC) with TiO_2 particles. The study demonstrated that Pickering emulsions stabilized by cCNC and TiO_2 particles can be prepared in two ways: layer by layer and conventional emulsification. The study contributed to better understanding of of the factors that influence emulsion formation and stability, which is crucial for their practical applications.

The formulation of these emulsions was only possible thanks to a thorough understanding of the TiO_2 properties gained within the thesis. The study of TiO_2 behaviour in media used for biocopmatibility testing, simulated body fluids, and human blood plasma revealed a significant impact of the media, mainly the presence of proteins on particle agglometarion. Here, the crystalline form of TiO_2 particles, in combination with composition of media, play important role. The form of TiO_2 particles also had significant impact on cytotoxicity. The findings of this study are decisive when considering the safety of TiO_2 in connection with oral and dermal exposure, which is freequent in cosmetics.

The next study included in the thesis significantly contributed to existing knowledge on systems that utilize cellulose combined with conducting polyaniline (PANI). Colloidal PANI dispersions prepared by dispersion polymerization in the presence of cellulose nanocrystals (CNC) or nanofibers (CNF) yielded PANI/CNC and PANI/CNF composites with promising biological properties, including antibacterial and antioxidation activity, as well as immunomodulatory effect on macrophages.

Novel Pickering emulsions containing undecane or capric/caprylic triglyceride oil were successfully formulated using the composite particles synthetized in the previous step. The work confirmed that the biological activity of the particles that stabilized the emulsions was preserved, and that the used oil (capric/caprylic triglyceride) introduced additional benefits to these systems. This approach is interesting for the application of such systems in biomedicine, particularly in the area of wound healing.

Finally, PANI/CNC and PANI/CNF colloids were used to fabricate conducting composite films *via* the *in-situ* dispersion polymerization. The films exhibited conductivity and antioxidation activity, both of which are essential for tissue engineering of electrically conducting tissues (cardiac, nerve). The biological tests showed that the films were not cytotoxic, and allowed cell proliferation comparable to the reference. Overall, this research provided a deeper understanding of the various conducting cellulose-based systems of new generation with interesting tunable properties that can be used in a variety of applications.

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LIST OF ABBREVIATIONS

AH	Aniline Hydrochloride
APS	Ammonium Persulfate
BC	Bacterial Cellulose
cCNC	Carboxylated Cellulose Nanocrystals
CE	Conventional Emulsification
CLSM	Confocal Laser Scanning Microscopy
CNC	Cellulose Nanocrystals
CNF	Cellulose Nanofibers
CP	Conducting Polymer
DMEM	Dulbecco's Modified Eagle's Medium
DPPH	1,1-diphenyl-2-picrylhydrazyl
E	Pickering Emulsion
e.g.	*exempli gratia*
EE	Encapsulation Efficiency
EHEC	Ethyl(hydroxyethyl) Cellulose
etc.	*et cetera*
EU	European Union
$FeCl_3$	Ferric Chloride
GA	Gum Arabic
H_2O	Water
H_2O_2	Hydrogen Peroxide
HCl	Hydrochloric Acid
HRP	Horseradish Peroxidase
i.e.	*id est*
IL-6	Inflammatory Cytokine Interleukin 6
in situ	In Its Original Place
in vitro	Withinthe Glass
in vivo	Within the Living
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
LD	Laser Diffraction
LPS	Lipopolysaccharides
MFC	Microfibrillated Cellulose
MIC	Minimum Inhibitory Concentration
n.d.	Not Determined
n.r.	Not Reported
NaCl	Sodium Chloride
NFC	Nanofibrillated Cellulose
NO	Nitric Oxide
NP	Nanoparticle
O/W	Oil-in-Water

OZP	Opsonized Zymosan Particles
PANI	Polyaniline
PBS	Phosphate-Buffered Saline
PE	Pickering Emulsion
PEDOT	Poly(3,4-ethylenedioxythiophene)
pH	Potential of Hydrogen
PPy	Polypyrrole
PT	Polythiophene
PVP	Polyvinylpyrrolidone
ROS	Reactive Oxygen Species
SC	Scavenging Activity
SD	Standard Deviation
SH	Sodium Hyaluronate
T	Caprylic/capric Triglyceride
TEM	Transmission Electron Microscopy
TEMPO	(2,2,6,6-Tetramethylpiperidin-1-yl)oxyl
TiO_2	Titanium Dioxide
via	Way
vs.	Versus

LIST OF UNITS

°C	Degree Celsius
g	Gram
g L^{-1}	Gram per Litre
h	Hour
M	Molarity (Mole per Litre)
mg	Milligram
min	Minute
mL	Millilitre
mN m^{-1}	Millinewton per Metre
nm	Nanometre
S cm^{-1}	Siemens per Centimetre
wt%	Percentage by Mass
µg mL^{-1}	Microgram per Millilitre
µm	Micrometre

LIST OF SYMBOLS

%	Percent
<	Less Than
>	Greater Than
°	Degree
β	Beta
γ^{AB}	Polar Parts of Surface Energy
γ^{LW}	Dispersive Parts of Surface Energy
γ^{tot}	Total Surface Energy
λ	Wavelength
π	Pi Covalent Bond

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LIST OF PUBLICATIONS

Publications in journal with impact factors

1. **Korábková, E.**; Kašpárková, V.; Jasenská, D.; Moricová, D.; Daďová, E.; Truong, T.H.; Capáková, Z.; Vícha, J.; Pelková, J.; Humpolíček, P. Behaviour of Titanium Dioxide Particles in Artificial Body Fluids and Human Blood Plasma. *Int. J. Mol. Sci.* 2021, **22**, 10614.

2. **Korábková, E.**; Kašpárková, V.; Vašíček, O.; Víchová Z.; Káčerová, S.; Valášková, K.; Urbánková, L.; Vícha, J.; Munster, L.; Skopalová, K.; Humpolíček, P. Pickering Emulsions as an Effective Route for the Preparation of Bioactive Composites: A Study of Nanocellulose/polyaniline Particles with Immunomodulatory Effect. *Submitted manuscript, under review.*

3. **Korábková, E.**; , Boeva, Z.; Radaszkiewiczc, K. A.; Skopalová, K.; Kašpárková, V.; Xu, W.; Pacherník, J.; Minařík, A.; Lindfors, T.; Humpolíček, P. Stimuli-Responsive Conductive Thin Film Composites of Conducting Polymers and Cellulose Nanocrystals for Tissue Engineering. *Submitted manuscript.*

4. **Korábková, E.**; Kašpárková, V.; Pacherník, J.; Minařík, A.; Valášková, K.; Káčerová, S.; Özaltin, K.; Moučka, R; Humpolíček, P. Conducting Composite Films Based on Polyaniline and Nanocellulose. *Prepared to submit.*

5. Urbánková, L.; Kašpárková, V.; Egner, P.; Rudolf, O; **Korábková, E**. Caseinate-Stabilized Emulsions of Black Cumin and Tamanu Oils: Preparation, Characterization and Antibacterial Activity. *Polymers*. 2019, **11**, 1951.

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1. **Korábková, E.**, D. Jasenská, T. H. Truong, J. Vajďák, Z. Capáková, V. Kašpárková, P. Humpolíček. Composite films of conducting polyaniline prepared in colloidal dispersion mode. In: *9th International Colloids Conference*. 2018, Sitges, Spain.

2. **Korábková, E.**, V. Kašpárková, A. Minařík, K. Valášková, S. Káčerová, K. Özaltin, R. Moučka, P. Humpolíček. Conducting composite films based on polyaniline and nanocellulose. In: *11th International Colloids Conference*. 2022, Lisbon, Portugal.

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Dispersion systems based on nanoparticles

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