Dialdehyde cellulose preparation, characterization and utilization as crosslinking agent for PVA

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Doctoral Thesis Summary

Tomas Bata University in Zlín

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Faculty of Technology

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Dialdehyde cellulose preparation, characterization and utilization as crosslinking agent for PVA

Příprava, charakterizace a využití dialdehydu celulózy jako síťovacího činidla pro PVA

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ABSTRACT

Solubilized dialdehyde cellulose (DAC) obtained from alpha cellulose modification via simple oxidation by sodium periodate was prepared and characterized. Immediately after preparation, solubilized DAC was stabilized by low pH in order to suppress degradation. The influence of DAC solubilization and its aging under acidic conditions on DAC properties was analysed. Molecular mass distribution (GPC), reactive aldehyde group content (titrimetry), crystallinity (XRD), vibrational spectra (FT-IR), thermal stability (TGA) and structural composition (LC-MS, NMR, SEM) were of the main interest. Furthermore, DAC was utilized as a suitable crosslinking agent for poly(vinyl alcohol) (PVA). The reactive aldehyde groups of DAC formed on the C2 and C3 carbons of anhydroglucopyranose unit serve as crosslinking counterparts for hydroxyl groups of PVA under acidic conditions. Appropriate catalyst system must be introduced to ensure formation of crosslinked acetal/hemiacetal bridged network of hybrid PVA/DAC hydrogels. Initially, two concentrations of catalyst system and different drying temperatures were chosen and their influences on the PVA/DAC xerogel and hydrogel properties were investigated by several analytical methods (FT-IR, XRD, TGA, network parameters etc.). Next, fresh and aged acidic DAC and two chemically distinct catalyst systems were employed in the crosslinking of PVA. The crosslinking effectivity and efficiency of these crosslinking systems (crosslinker + catalyst) were investigated in the terms resulting PVA/DAC hydrogel properties, i.e. crystallinity (XRD) and stiffness (tensile testing) of the dried gel, furthermore structural and functional network parameters of swollen gels were characterized. Finally, comparison between DAC and glutaraldehyde (GA) crosslinker was carried out using broad range of these PVA crosslinkers with subsequent evaluation of network parameters of prepared PVA/DAC and PVA/GA hydrogels. Acidified DAC exhibited the capability to act as an effective crosslinker for PVA with the resulting hydrogel properties dependent on the choice of concentration of catalyst system and the drying temperature. Moreover, it was found that the properties of PVA/DAC are governed by the molecular weight of used DAC. The acidic condition retains DAC usability as a crosslinking agent even after 28 days from its preparation. It was found that DAC possesses exceptional crosslinking efficiency at very low concentrations compared to GA and enables formation of hydrogels of very high swelling capacity. This behaviour arises from DAC macromolecular character as it forms “two-phase” network topology containing regions of very high crosslink density adjacent to DAC chains embedded in a matrix formed by linear parts of PVA macromolecules.

ABSTRAKT

Byl připraven a charakterizován solubilizovaný dialdehyd celulózy (DAC) získaný modifikací alfa celulózy pomocí jodistanové oxidace. Za účelem potlačení degradace byl solubilizovaný DAC stabilizován nízkým pH ihned po jeho přípravě. Byl zkoumán vliv solubilizace a stárnutí v kyselém prostředí na vlastnosti DAC. Hlavními předměty zájmu byla zkoumání distribuce molekulových hmotností (GPC), obsahu reaktivních aldehydových skupin (volumetrie), vibračních spekter (FT-IR), tepelné stability (TGA) a strukturního složení (LC-MS, NMR, SEM). Dále byl DAC použit jako síťovací činidlo pro polyvinylalkohol (PVA). Reaktivní aldehydové skupiny DAC vytvořené na pozicích C2 a C3 anhydroglukopyranózové jednotky slouží jako síťovací protějšky k hydroxylovým skupinám PVA v kyselých podmínkách. K zajištění vzniku sítě hybridního PVA/DAC hydrogelu tvořeného acetalovými/hemiacetalovými můstky musí být zaveden vhodný katalytický systém. Zpočátku byl zkoumán vliv dvou vybraných koncentrací katalytického systému a zvolených teplot sušení na vlatnosti PVA/DAC xerogelů a hydrogelů pomocí několika analytických metod (FT-IR, XRD, TGA a parametry sítě). Poté se k síťování PVA použil kyselý roztok DAC o různém stáří společně se dvěmi chemicky odlišnými katalytickými systémy. Síťovací efektivita a účinnost těchto různých síťovacích systémů (síťovadlo + katalyzátor) byly zkoumány z hlediska vlastností výsledných PVA/DAC hydrogelů, tj. krystalinity (XRD) a tuhosti (tahové zkoušky) vysušeného gelu, a dále strukturních i funkčních parametrů nabotnalé sítě. Nakonec bylo provedeno srovnání mezi síťovacími činidly DAC a glutaraldehydem (GA) v širokém rozsahu jejich koncentrací s následným vyhodnocením parametrů sítě připravených PVA/DAC a PVA/GA hydrogelů. DAC udržovaný při nízkém pH vykazuje schopnost působit jako účinné síťovací činidlo pro tvorbu PVA hydrogelů o výsledných vlastnostech závislých na koncentraci katalytického systému a teplotě sušení. Bylo zjištěno, že vlastnosti PVA/DAC jsou řízeny molekulovou hmotností použitého DAC. Podmínky nízkého pH zachovávají použitelnost DAC jako síťovacího činidla i po 28 dnech od jeho přípravy. DAC vykazuje výjimečnou účinnost síťování PVA ve velmi nízkých koncentracích ve srovnání s GA a umožňuje tak tvorbu hydrogelů s velmi vysokou schopností bobtnání. Toto chování je projevem makromolekulárního charakteru DAC, jenž vytváří "dvoufázovou" topologii sítě obsahující oblasti s velmi vysokou hustotou zesíťování PVA v blízkosti řetězců DAC vložených do matrice tvořené lineárními částmi PVA makromolekul.

1. INTRODUCTION

Biopolymer-based materials are at the peak of interest for many scientists due to the growing demand of society to reach the goal of sustainable development via utilization of renewable and worldwide occurring substances with presumable lower impact on environment and living organisms. Biopolymer is by definition a macromolecular substance, which is naturally synthesized, often biodegradable and usually exhibits low toxicity. Cellulose, starch, chitosan, gluten or collagen meets this definition and therefore they are exhaustively used in a plethora of various applications in fields of medical, packaging, food and agricultural sector. [1] These plant- and animal-based biopolymers commonly exhibit hydrophilicity, which imparts water retention capability and thus these materials are frequently used as additives or just as pure substances themselves. The valuable property of water retention emerges as result of presence of three-dimensional network of crosslinked macromolecules containing hydrophilic side groups [2]. Such structures are generally known as hydrogels. Hydrogels should by definition possess (i) macromolecules of at least one polymeric substance joined by covalent bonds, and/or (ii) macromolecular entanglements resulting in physically crosslinked units, (iii) strong van der Waals interactions or hydrogen bonds between polymer chains, or (iv) crystallites composed of at least two macromolecular chains. [3]

Potentially, hydrogels can be prepared by the combination of appropriate biopolymer or biopolymer-based substance with synthetic polymer. Based on the natural origin of biopolymer component, these materials can be further employed in the field of biomedical sciences as they can mimic the living tissue structure; [4–6] or possess modified biodegradability profile. [7] Furthermore, if hydrogels are intended for utilization in pharmaceutics they should exhibit low toxicity and biocompatibility so they can be utilized as wound dressing materials containing active substance for improved healing of wounds, various body implants such as cartilages, drug delivery systems with tuneable release profile, scaffolds for better tissue regeneration and many others. [8–11]

Poly(vinyl alcohol) (PVA) is one of the synthetic polymers suitable or the preparation of hydrogels. There are several approaches how to achieve crosslinked PVA-based hydrogels utilizing physical or chemical routes. For example, PVA hydrogels can be obtained by physical crosslinking (reversible hydrogels) induced by cyclic freeze-thawing [12]. However, such crosslinking process exhibits relatively poor definition of the chemical reaction mechanism although it is advantageous as no additive compound is needed. Next, the hydroxyl groups of PVA enable formation of chemical crosslinks (permanent hydrogel) when various aldehydes, anhydrides or boric acid are used as crosslinking agents. [1, 12–14] The disadvantage of this approach lies in the relatively high toxicity of these low molecular crosslinkers. Particularly, it is

their high reactivity and synthetic origin (except boric acid) that causes high cytotoxicity and enables readily penetration through various portals of entry into living organism.

Thus, to fulfil the requirements on the fabrication of non-toxic and biocompatible hydrogels suitable for pharmaceutical or medical applications, it is preferable to employ crosslinking agent based on or derived from biopolymers. This allows to obtain materials with low toxicity as well as to reduce the impact on environment and living organisms. Partial progress in this field was accomplished by introducing naturally available low toxic crosslinker Genipin. This substance is produced by the enzymatic extraction from the fruits of *Gardenia Jasminoides*. However, the drawbacks of its mass utilization can be found in its limited availability and therefore relatively high cost. [15] It is more desirable to perform specific derivatization of abundant and easily available biopolymers and thus introducing new functional groups on polymer backbone. One of many potential candidates for this purpose is cellulose as it offers broad possibility of modifications resulting in number of various derivatives. [16]

In the theoretical section of this Thesis, the literature review on the topic of cellulose and its oxidation, especially dialdehyde cellulose (DAC), was carried out. Furthermore, background of PVA hydrogel preparation, characterization and utilization is discussed. In the first part of experimental section, dialdehyde cellulose (DAC) prepared from alpha cellulose by simple sodium periodate oxidation of hydroxyl groups to aldehyde groups was utilized as a crosslinking agent for PVA. The results of this pilot study have shown potential of DAC towards these purposes. [17] DAC solution was blended with commercially available poly(vinyl alcohol), forming PVA/DAC hydrogels. Effects of two different concentrations of catalyst systems based on the mixture of sulfuric acid, methanol and acetic acid were studied, as they represent one possible catalyst system for crosslinking reactions of aldehyde moiety. [18] To optimize the process of PVA/DAC preparation, the influence of drying temperature on hydrogel physical properties was investigated. In the second part, insolubilized and solubilized form of prepared DAC was investigated with respect to crosslinking application. Furthermore, the process of DAC solubilization was investigated and the product was analysed during four week of its aging. Due to known DAC sensitivity towards alkalic environment, the DAC solution was kept under acidic condition for the first time. The last part of this Thesis deals with the application of DAC as a PVA crosslinking agent. This includes utilization of fresh and aged DAC with subsequent analysis of properties of prepared PVA/DAC hydrogels. Moreover, two chemically distinct catalyst systems were introduced to initiate crosslinking reactions and their influence was evaluated. Next, in order of DAC crosslinking effectivity and efficiency assessment, this novel macromolecular crosslinking agent was compared to commonly used low molecular crosslinker glutaraldehyde and the properties of resulting hydrogels were compared in the terms of network parameters.

2. CELLULOSE

Cellulose is undoubtedly the most abundant and widely used organic macromolecular substance in the world. It represents linear macromolecular chains consisting of D-anhydroglucopyranose units linked by β-1,4-glycosidic bonds. Cellulose occurs naturally in various species of higher vascular plants (seed hairs of cotton – 95 %; bast fibres of flax, hemp, sisal, jute and ramie – 60 to 80 %; wood – 40 to 55 %), lower non-vascular plants (algae, lichen and fungi) and other organisms like tunicates and bacteria. [19–22] For this reason, it is identified as a renewable biopolymer, a substance synthetized by living organisms.

2.1 Structure and properties

On molecular level, cellulose macromolecules consist of β-1,4-linked D-anhydroglucopyranose units (AGU) established in chair conformation. Figure 1 depicts molecular structure of cellulose with marked parts. [23]

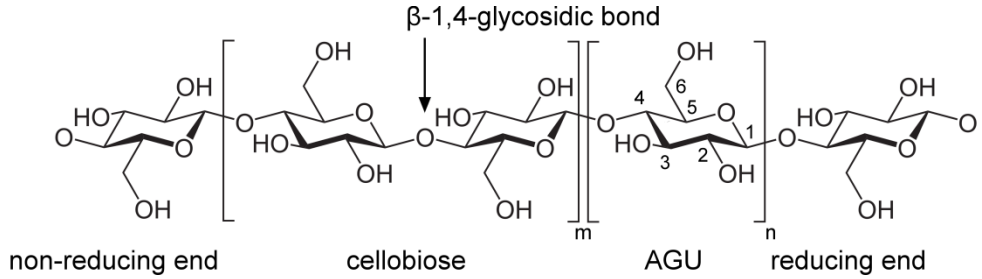

Figure 1 *Representation of cellulose constituted of cellobiose units or AGUs (with atom numbering) via β-1,4-glycosidic bonds, non-reducing and reducing end of polymer.*

From the supramolecular level point of view, pure cellulose has been identified in the number of different crystal polymorphs (type **I**, **II**, **III** and **IV**). [23, 24]

Finally, morphological level is defined as organization of crystals into microfibrils. Microfibrils consequently form fibrillary structures, layers, cell walls, tissues etc. [16, 20, 23]

Molecular, supramolecular and morphological levels impart mechanical, thermal and chemical properties of cellulose. Related to cellulose properties, it possesses other typical properties such as hydrophilicity, chirality, biodegradability and relatively high chemical reactivity potential due to the donor ability of hydroxyl groups. In contrast to synthetic polymers, cellulose exhibits extraordinary polyfunctionality, high level of chain rigidity and sensitivity to hydrolysis and oxidation. [20]

2.2 Oxidation induced cellulose derivatives

Arising from the presence of the three hydroxyl groups bonded on C6 (primary), C2 and C3 (secondary) positions in AGU (Figure 2), cellulose offers a broad variety of possible modifications via different derivatizations, i.e. esterification (xanthanation, acetylation and nitration) and etherification.

Furthermore, hydroxyl groups of AGU can enter oxidation reactions. [23, 25] The partial oxidation processes of cellulose are considered as long-standing goal in cellulose chemistry, since they provide access to novel products and intermediates with valuable properties. In general, such materials are considered insoluble in water, although there are exceptions. [24–26]

The complexity of cellulose oxidation emerges from the (i) different reactivity of three available hydroxyl groups per AGU, (ii) different accessibility of regions of cellulose present in crystalline or amorphous form and (iii) choice of oxidizing agent. [23] This complexity results in a plethora of various possible products of oxidation, which are generally described as oxycellulose (see Figure 2). [25]

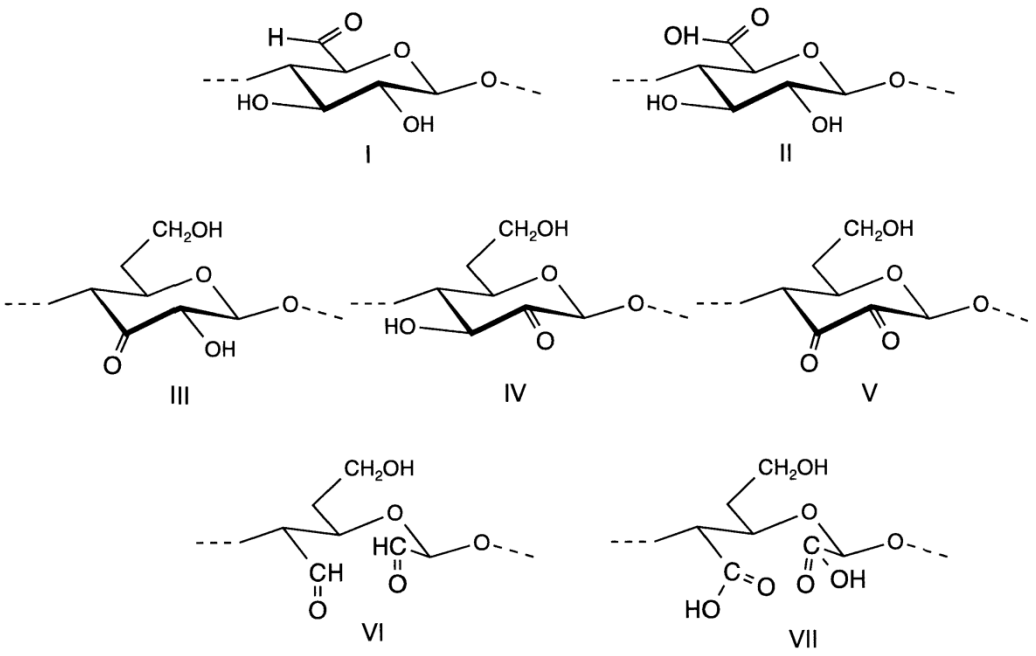

Figure 2 *Possible structures of oxycellulose repeating units. [25]*

Oxycelluloses are mainly utilized in medicine and pharmacy as (i) haemostatic agents, (ii) wound dressing materials, (iii) antibacterial agents, (iv) postoperative adhesion agents or (v) enterosorbents. [27] Other pharmaceutical applications involve usage as drug carriers, as a scaffolds in tissue engineering or as materials suitable for enzyme immobilization. [28–33]

3. DIALDEHYDE CELLULOSE

The oxidation of cellulose by periodate salts has been known for long time [34, 35] and is highly regioselective without significant side reactions. [36] Resulting product of periodate oxidation of cellulose is referred to as 2,3-dialdehydecellulose or simplified to dialdehyde cellulose, commonly abbreviated as DAC.

3.1 Preparation

One of the main advantages of DAC preparation lies in the relative simplicity of the process. In general, aqueous solution of sodium periodate ($NaIO_4$) is mostly used as the cellulose periodate oxidizing agent [37–39], although potassium periodate is also reported [40]. It is recommended to carry out this oxidation in dark. [25, 41, 42] The mechanism of periodate oxidation of 1,4-linked glucans is shown in Figure 3.

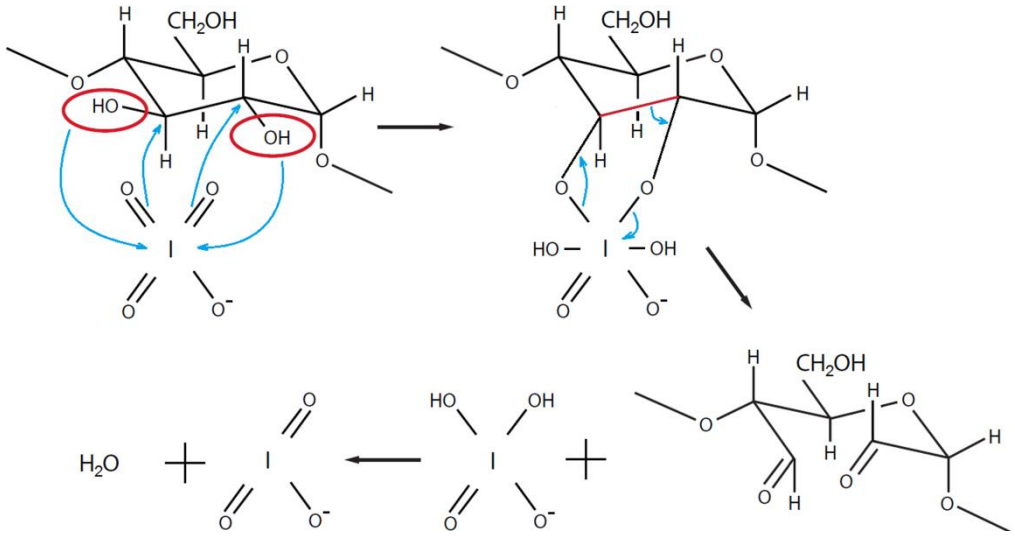

Figure 3 *Mechanism of periodate oxidation of cellulose AGU. [43]*

This method produces solid state DAC. Nevertheless, it is possible to prepare aqueous solution of DAC of high degree of oxidation by the methods of prolonged heat assisted solubilization in water. Solubilized DAC could be afterwards utilized in solution based processes. [44, 45]

3.2 Structure and properties

The mechanism of periodate oxidation (see Figure 3) shows the resulting molecular structure of DAC product. The secondary hydroxyl groups of AGU are converted to pair of aldehyde groups along with the cleavage of C2–C3 bond. However, free aldehyde groups in DAC (**A** in Figure 7) are present in very

limited amount as the highly reactive aldehyde groups tend to stabilize them self. Instead of free aldehyde form, a mixture of several DAC forms noted in Figure 4 were proposed [35] and some confirmed by solid-state NMR [46].

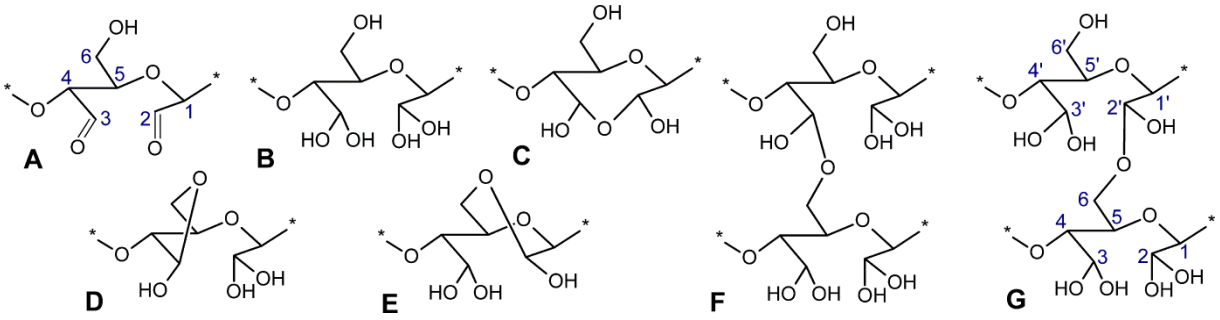

Figure 4 *Possible structural arrangements of DAC. A – dialdehyde, B – fully hydrated dialdehyde, C – hemialdal, D – intramolecular hemiacetal with C3–O–C6 bond, E – intramolecular hemiacetal with C2–O–C6 bond, F – intermolecular hemiacetal with C6–O–C3'bond, G – intermolecular hemiacetal with C6–O–C2' bond. Intermolecular hemiacetals F and G may also contain hemialdal unit C in their structure (not shown). [47]*

The reactive aldehyde group content can be determined utilizing Schiff base reaction of aldehyde group with hydroxylamine hydrochloride resulting in formation of oxime. [46, 48] The hydrochloric acid liberated from this reaction can be quantitatively assessed by titration. Therefore, the conversion of aldehyde to oxime can be easily determined by the consumption of alkali. [44, 49] Fully oxidized DAC contains 12.5 mmol of aldehyde groups per gram [44].

The changes in the cellulose chemical structure after periodate oxidation to DAC are manifested in infrared spectrum by band at 1740 cm^{-1} representing the carbonyl groups vibrations. Besides this specific band, another peak at 880 cm^{-1}, signifies the hemiacetal or hydrated DAC form. [46]

The scission of C2–C3 bond induced by the periodate oxidation results in the opening of the AGU ring which is further reflected in the destruction of otherwise ordered packing of cellulose chains. [46, 50] The decrease of crystallinity due to partial destruction of AGU units proceeds hand in hand with the loss of thermal stability.

Another very important property, the stability of DAC in time, should be addressed before any consideration of practical use. When DAC is kept in non-dried state, the reactivity dramatically decreases to 68 % after only one week from preparation [51]. Different study showed decrease of reactive aldehyde group content about 15 % as well as the steady decrease of molecular weight about 50 % after 3 weeks of preparation of fully oxidized DAC solubilized under various conditions [44].

The solubilization processes of DAC used within the study of Kim *et al.* (2004) showed to have low impact on the molecular weight of DAC prepared

from microcrystalline cellulose Funacel SF. [44] However, the study of Sulaeva *et al*. (2015), which was mainly focused on the characterization of molecular weight of solubilized DAC from another source of microcrystalline cellulose Avicel PH-101 and cotton linters, showed somewhat contradictory results to those made by Kim *et al*. (2004). [45] Their findings are summarized in Table 1.

Table 1 *Mass average molecular weight ($\bar{M}_w$) values of source cellulose material and DAC after defined process of solubilization. [44, 45]*

Source	$\bar{M}_{w\ \text{source}}$ (kDa)	DAC sol. (time, temp.)	$\bar{M}_{w\ \text{sol. DAC}}$ (kDa)	$\bar{M}_w$ loss (%)
Funacel SF	42.7	4 h, 80 °C	41.2	3.5
		6 h, 80 °C	39.2	8.2
		1 h, 100 °C	42.0	1.6
		2 h, 100 °C	30.4	28.8
Avicel PH-101	40	1 h, [a]	19.7	50.8
Cotton linters	180	1 h, [a]	23.6	86.9

[a] Not specified, heated at reflux.

DAC, whether solubilized or not, was reported to be rather unstable in time especially when kept in alkaline solution. [45, 52] The degradation processes identified as β-elimination were well described by Veelaert *et al*. (1997) and Potthast *et al*. (2009). [49, 52] The pH of DAC suspension or solution seems to be one of the key parameters when optimizing the stability.

3.3 Applications of DAC

The presence of highly reactive aldehyde groups on DAC backbone imparts its usage as cellulose based column packings in aqueous chromatography, [53–55] heavy metal ion and dyes absorbent, [26, 56, 57] flocculation agent, [58] protein immobilization material, [59–61] drug delivery carrier, [62–64] material in tissue scaffold engineering, [65] or in graft copolymerization. [66] Furthermore, the recent studies of solubilized DAC showed its potential as a suitable low toxicity crosslinking agent for chitosan [67, 68].

In general, aldehyde groups promise a broad follow-up chemistry as it can be modified to carboxylic acid, [26, 69, 56, 70, 71] primary alcohols, [69, 70] imines, [37, 50] or sulfonates. [72] Both DAC and its derivatives possess a great potential in high-end applications such as medical materials [67, 73] and biodegradable composites. [74]

4. POLY(VINYL ALCOHOL) BASED HYDROGELS

Poly(vinyl alcohol) (PVA) is undoubtedly one of the most frequent and used material for hydrogel applications as it possesses valuable properties such as biocompatibility, biodegradability, relatively low toxicity and it is possible to blend it with a broad range of synthetic polymers or biopolymers. [11]

Hydrogels are by definition three-dimensional, hydrophilic, polymeric crosslinked network structures capable of absorbing large amounts of water. [75] Network of hydrogel is generally composed of homo- or copolymers, which is insoluble due to the presence of chemical or physical crosslinks. [76] The essential classification of hydrogels includes two categories:

(i) Permanent (chemical) hydrogel: covalently crosslinked network, which contains stable covalent bonds between macromolecules (besides the hydrogen bonds). [77, 78]

(ii) Reversible (physical) hydrogel: molecular entanglements, secondary forces such as ionic, hydrogen bonding or hydrophobic interactions are responsible for the network formation. The change in physical conditions or application of stress causes disruption of these reversible interactions. [77, 78]

Besides above mentioned categorization, hydrogels can be classified on the base on their other properties such as degradability, response to external stimuli, ionic charge and many others. [8]

4.1 PVA hydrogel formation: Physical and chemical routes

Physical type of approach has the undeniable advantage in omitting any kind of crosslinking agent. However, the crosslinking process is rather poorly defined in the term of chemical reaction mechanism and includes methods:

(i) Freeze-thaw induced crystallization. The crosslinking of PVA is induced by formation of crystalline regions by cyclic heating and freezing (-20/+25 °C), these regions then act as physical crosslinks. [79]

(ii) Heat treatment. Partial degradation due to higher temperatures produces unsaturation, chain scission and thus chemical crosslinks. [12]

(iii) Irradiation. Radiation induced crosslinking exhibit looser, more open structure. [12]

Characteristic feature of all chemical crosslinking routes is the utilization of crosslinking agent. The crosslinking is achieved by the reaction of functional hydroxyl groups of PVA and crosslinking agents such as aldehydes (formaldehyde, glutaraldehyde, acrolein etc.), [80, 81] di- tri- and polycarboxylic acids, [82] anhydrides, [83] alkoxysilanes [84] and many others. [12, 85–87] The common characteristic for these crosslinking agents is the synthetic origin and subsequent high toxicity. Thus, the resulting hydrogels should be intensively wasted prior to use in medical sector.

4.2 Characterization and network parameters

The evaluation of properties of hydrogels is often expressed by the network parameters which can be calculated with the aid of equilibrium swelling theory suggested by Flory and Rehner (1943). [88] The crucial and the most important parameters of network are percentage of swelling, equilibrium water content (EWC), gel fraction, average molecular weight between crosslinks ($\bar{M}_c$) and crosslink density (ρ_c). [88–92]

4.3 Applications of PVA hydrogels

There are myriad of specific applications of crosslinked PVA hydrogels in many various fields. The properties of PVA hydrogels are often tailored by addition of other synthetic polymer or biopolymer.

The work of Kamoun *et al*. (2014) summarizes the wound dressing applications of PVA based hydrogel combined with numerous natural and synthetic polymers. [11]

Several other important applications of PVA hydrogels are within the medical sector. The review on the utilization of PVA hydrogels by Baker *et al*. (2012) outlines the most widespread usage of this material in soft contact lenses, artificial cartilages, orthopaedic applications and other medical devices. [10]

Another valuable source on the usage of PVA hydrogels in the form of membranes designed for variety of water treatment applications is the work of Bolto *et al*. (2009). These applications include micro-, ultra- and nano-filtration, reverse osmosis, pervaporation etc. It offers deep insight into the possible methods of PVA crosslinking and its subsequent specific applications. [12]

Besides above mentioned reviews, there are number of reports in the Web of Science database (WoS) in recent years (2013–2017) regarding the characterization and utilization of PVA-based hydrogels. These examples can be divided in several topics such as the most cited articles relevant for:

- Medical sector applications:
  PVA/cellulose nanowhiskers (CNWs) freeze-thawed hydrogels with controlled porosity, morphology and barrier properties suitable for wound dressing application [93].

- Water treatment applications:
  Reusable high capacity PVA/gelatine hydrogel beads crosslinked by boric acid utilized for Pb^{2+} removal driven by chemisorption with ion-exchange mechanism [94].

- Self-healing and shape memory hydrogels:
  PVA/graphene oxide memory shape nanocomposite with strong H-bonding interaction between PVA and graphene oxide [95].

5. AIM OF DOCTORAL THESIS

The current work deals with research and development of a biopolymer-based crosslinking agent for polymers containing hydroxyl groups on their backbone. Cellulose derivative and poly(vinyl alcohol) were selected as the starting materials. The aim of the Thesis was study of dialdehyde cellulose preparation, characterization and its utilization as a crosslinking agent for PVA. It was defined according to challenge identified with respect to the studied field, performed literature review and preliminary experiences.

Particularly, the aim includes preparation of DAC by a suitable technique, optimization of the method of its preparation, study of its structure, properties and aging, and its applicability as crosslinker in the preparation of PVA hydrogels. Furthermore, this study includes an optimization of the crosslinking process with respect to the properties of final hydrogel material and a comparative crosslinker study, in which the properties (namely network parameters) of hydrogel materials prepared using DAC are compared to those of hydrogels prepared using common crosslinking agent (glutaraldehyde).

This aim may be achieved by accomplishment of the following objectives:

- Research of cellulose oxidation to prepare its reactive derivative (namely DAC) with potential use as a crosslinking agent for PVA.

- Elucidation of structure of prepared DAC via suitable analytical methods, particularly in solution.

- Research of stability (including eventual stabilization if discovered) of prepared DAC in its application form (i.e. solution) in time. Characterization of changes in the structure with aging.

- Development of a crosslinking system, namely choice and suitability of crosslinking catalysts, process parameters (i.e. drying temperatures) and evaluation of their influence on properties crosslinked materials.

- Investigation of crosslinking capability of fresh and aged crosslinking agent and influence of catalyst choice on material properties of resulting hydrogels.

- Comparative study on PVA crosslinking utilizing common crosslinking agent (i.e. glutaraldehyde) and DAC under equal conditions, evaluation of crosslinking efficiency of used crosslinkers on resulting hydrogel properties in the terms of network parameters comparison.

6. EXPERIMENTAL

6.1 Materials, Sample preparation and Experimental methods

DAC was prepared from alpha cellulose (Sigma Aldrich, Co.) by periodate oxidation using sodium periodate ($NaIO_4$). Purified solid DAC was solubilized under various initial pH conditions (3.5–7.5, samples designated "W"–"Z", respectively) utilizing different time of solubilizaton (0.5–7 h) and different methods of heating (conventional vs. microwave assisted). Ethylene glycol, sodium hydroxide (NaOH), hydrochloric acid (HCl), hydroxylamine hydrochloride and sodium chlorite ($NaClO_2$) were utilized in DAC preparation and characterization.

Two types of PVA were employed in crosslinking reactions; Mowiflex TC 232 (Kuraray Specialities, Europe GmbH) Mowiol 84–86% hydrolysed (Sigma Aldrich Co.). Two chemically distinct catalyst systems base on A) HCl and B) 10vol% solutions of sulfuric acid (H_2SO_4), methanol (CH_3OH), acetic acid (CH_3COOH) were used.

All components of B) catalyst system were initially tested in "Pilot study" for crosslinking of "Mowiflex" type of PVA by 2 wt% of fresh DAC using two different concentrations noted as "PVA/DAC set 1" and "PVA/DAC set 2" and different drying temperatures (see Table 2).

Table 2 *PVA/DAC "Pilot study" samples designation based on different amount of catalyst system and different drying temperatures. Volumes of catalyst system components are from their 10vol% solutions. [17]*

Sample series	**PVA/DAC set 1**		**PVA/DAC set 2**	
Catalyst system composition per sample	1 mL H_2SO_4 1.5 mL CH_3OH 3 mL CH_3COOH		0.25 mL H_2SO_4 0.5 mL CH_3OH 0.75 mL CH_3COOH	
Drying temp. (°C)	**unwashed**	**washed**	**unwashed**	**washed**
90	1-90-U	1-90-W	2-90-U	2-90-W
60	1-60-U	1-60-W	2-60-U	2-60-W
30	1-30-U	1-30-W	2-30-U	2-30-W

Fresh/aged DAC was utilized in 1 wt% concentration in the crosslinking of "Mowiflex" PVA type using both chemically distinct catalyst systems (A – 1.5 mL of 1.33*M* HCl per sample, B – same as in Table 2 "PVA/DAC set 2"). Designation of samples prepared using aged DAC and two types of catalyst systems are noted in Table 3. All prepared hydrogels were dried at 30 °C, washed and analysed.

Table 3 *PVA/DAC samples prepared using aged DAC. [43]*

DAC age (days)	PVA/DAC blend A	PVA/DAC blend B
1	A01	B01
14	A02	B02
28	A03	B03

Furthermore, fresh DAC was utilized in broad range of concentration for crosslinking of both types of PVA. Analogously, 50% water solution of glutaraldehyde (GA) crosslinker was used (with the respect to same amount of reactive aldehyde group per sample). Resulting PVA/DAC and PVA/GA hydrogels were prepared with the aid of catalyst A) and are noted in Table 4.

Table 4 *PVA/DAC and PVA/GA samples prepared using different PVA source and different crosslinker (DAC or GA). Equal conditions are expressed by the amount of reactive group (n_{-CHO}) per sample. [43]*

n_{-CHO} per sample	DAC crosslinker			GA crosslinker		
	DAC	PVA/DAC		GA	PVA/GA	
(μmol)	(wt%)	Mowiflex	Mowiol	(μL)	Mowiflex	Mowiol
2920	5	DTC-A	DSA-A	233	GTC-A	GSA-A
1750	3	DTC-B	DSA-B	240	GTC-B	GSA-B
877	1.5	DTC-C	DSA-C	69.9	GTC-C	GSA-C
585	1	DTC-D	DSA-D	46.6	GTC-D	GSA-D
146	0.25	DTC-E	DSA-E	11.6	GTC-E	GSA-E
73.1	0.125	DTC-F	DSA-F	5.8	GTC-F	GSA-F
36.6	0.0625	DTC-G	DSA-G	2.9	GTC-G	GSA-G

All chemicals used in the preparation of DAC and catalyst systems were of analytical quality and were purchased from PENTA, Czech Republic, with the exception of GA, CH_3COOH, $NaClO_2$ and hydroxylamine hydrochloride (Sigma Aldrich, Co.). Demineralized water was used throughout the experiment.

Insolubilized, solubilized-dried and solubilized DAC samples were analysed by several analytical methods, such as by infrared (IR) spectroscopy (FT-IR), thermogravimetric analysis (TGA), X-ray diffraction analysis (XRD), liquid chromatography-mass spectral analysis (LC-MS), nuclear magnetic resonance (NMR), viscosity and density measurements, scanning electron microscopy (SEM), gel permeation chromatography (GPC) and reactive aldehyde content. Prepared PVA xero- and hydrogel materials were analysed by IR spectroscopy (FT-IR), thermogravimetric analysis (TGA), X-ray diffraction analysis (XRD), solid-state nuclear magnetic resonance (CP/MAS ^{13}C NMR), tensile measurements, network parameters and macroscopic observation. [43, 47]

7. SUMMARY OF RESULTS, DISCUSSION AND CONCLUSIONS

The summary of results, discussion and conclusions can be divided into three key parts following the structure of the Thesis:

(i) Initially, the pilot study demonstrated the possibility of solubilized DAC utilization as a crosslinking agent for PVA. It was found that one of the key factors defining the resulting PVA/DAC material properties is the optimization of process parameters such as catalyst system concentration and drying temperature. Within this pilot study, the crosslinking of PVA matrix was achieved in all hydrogel samples prepared by employing 2 wt% of DAC crosslinking agent, both concentrations of catalyst system based on sulfuric acid and whole set of drying temperatures. Resulting materials possessed different network parameters (see Figure 5) and exhibited different thermal behaviour (see Figure 6) based on the variation of these process parameters.

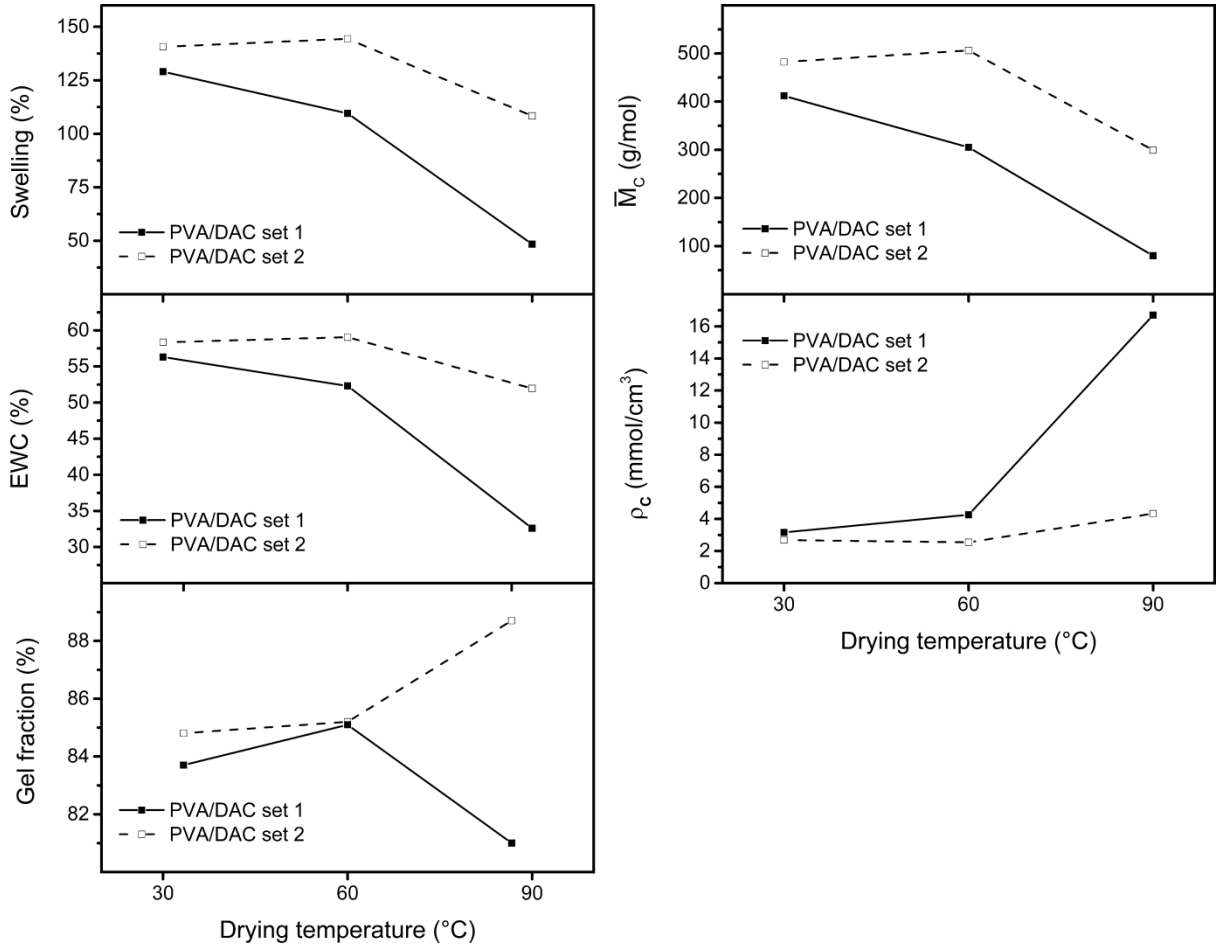

Figure 5 *PVA/DAC network parameters dependence on drying temperature and used concentration of catalyst system (pilot study). The lines connecting points in the right graph are only guides for eyes.*

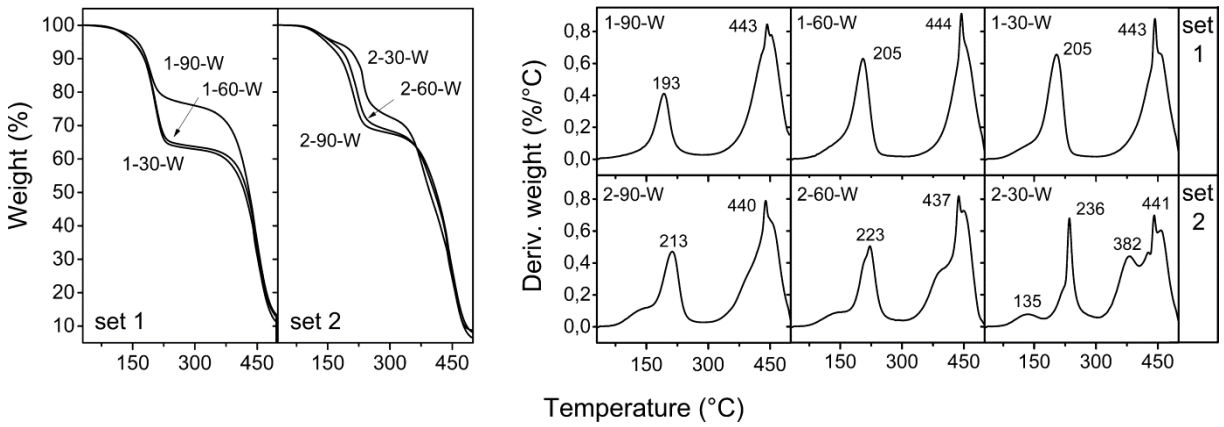

Figure 6 *TGA analysis of PVA/DAC xerogels prepared within pilot study. [17]*

However, in order to obtain degradation-free hydrogel material (see Figure 7), the optimal parameters for the preparation of the PVA/DAC crosslinked material should include drying temperatures below 60 °C and utilize lower concentration of catalyst system. [17]

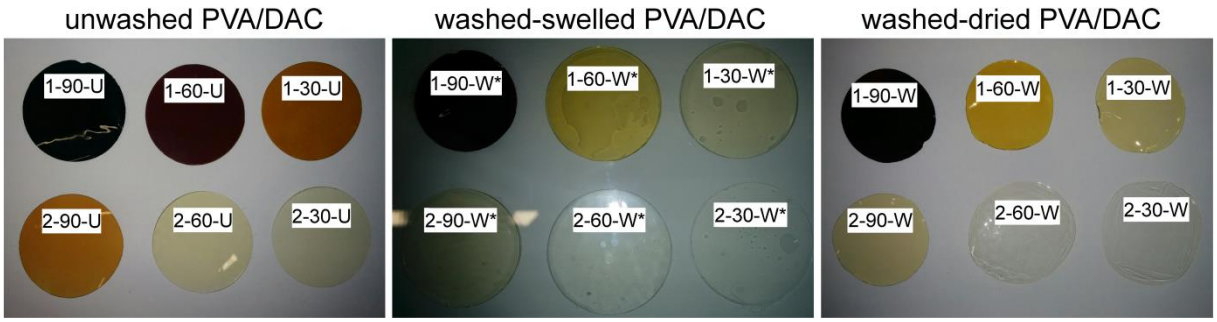

Figure 7 *PVA/DAC xerogels prepared within pilot study. [17]*

(ii) The next part focused on the process of DAC preparation, analysis and detailed investigation of its solubilization process. The initial characterization of prepared DAC confirmed presence of reactive aldehyde groups (1730 and 875 cm^{-1}) and disruption of ordered macromolecular packing manifested by decrease in crystallinity compared to original cellulose (see Figure 8). [17, 47]

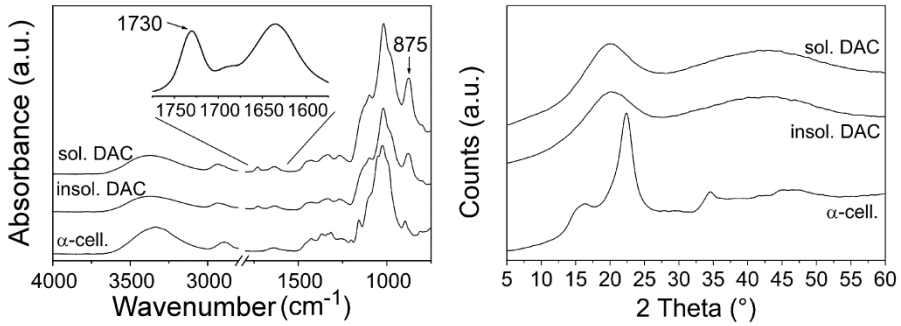

Figure 8 *FT-IR and XRD analysis of cellulose, insolubilized and solubilized-dried DAC. [17, 47]*

In the subsequent step, it was found that the DAC solubilization process causes severe degradation of the material regardless of chosen heating method or initial pH. This is demonstrated in Table 5 summarizing the average weight molecular weight evolution during solubilization using conventional heating method.

Table 5 *DAC solubilization analysis under different initial pH conditions.*

Initial pH (-)	**#**	**Solub. time (hour)**	**Solub. content (mg/mL; %)**	**pH (-)**	$\bar{M}_w$ **(g/mol)**	**PDI (-)**
	W05-f	0.5	0; 0	3.5	-	-
	W1-f	1	0.45; 0.8	3.8	6 600	1.89
3.5	W3-f	3	0.57; 1.1	3.5	6 800	1.89
	W5-f	5	0.76; 1.4	3.5	6 900	2.03
	W7-f	7	1.27; 2.4	3.6	6 900	2.03
	X05-f	0.5	1.48; 3.1	3.8	1 800	1.64
	X1-f	1	7.32; 15.2	3.5	8 500	2.58
5	X3-f	3	12.67; 26.2	3.5	9 800	2.45
	X5-f	5	28.1; 58.2	3.5	10 700	2.55
	X7-f	7	45.54; 94.3	3.6	9 400	2.47
	Y05-f	0.5	1.67; 3.2	4.5	1 600	1.6
	Y1-f	1	8.32; 15.5	4.1	9 100	2.6
6	Y3-f	3	18.81; 35.5	3.5	10 700	2.55
	Y5-f	5	31.74; 60	3.2	10 600	2.75
	Y7-f	7	51.25; 96.8	3.4	9 100	2.39
	Z05-f	0.5	10.97; 22	4.5	1 400	1.56
	Z1-f	1	33.13; 66.4	4.4	6 600	2.44
7.5	Z3-f	3	44.05; 88.3	3.8	6 500	2.83
	Z5-f	5	45.44; 91.1	3.5	5 000	2.38
	Z7-f	7	49.12; 98.4	3.6	4 300	2.26

Thus the contradictions in literature between the studies of Kim *et al.* (2004) [44] and Sulaeva *et al.* (2015) [45] were decided in the favour of progressive deterioration of DAC macromolecules during its solubilization. The resulting product of solubilization exhibited approximately one tenth of the original cellulose polymerization degree. It seems that the solubilization goes simultaneously with degradation of DAC chains and can be ascribed to the scission of macromolecular DAC fragments loosen from the gradually dissolving solid phase of insolubilized DAC particles as schematically depicted in Figure 9.

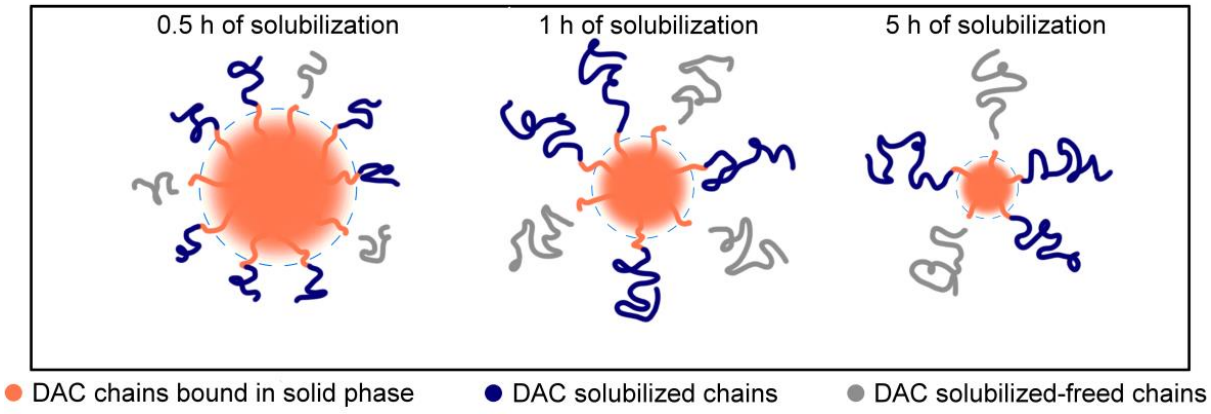

Figure 9 *Schematic representation of DAC solubilization with the respect to its time, size of insolubilized DAC phase and size of macromolecular fragments.*

The evolution of morphology of DAC particles during solubilization is exemplified in Figure 10 for the two extreme cases of used initial pH (3.5 and 7.5). The images correspond to the series of data noted in Table 5. In brief, the higher the initial pH is, the faster is the particle dissolution. After complete solubilization and lyophilisation, the DAC forms mostly spherical beads (SEM images not shown in this Summary).

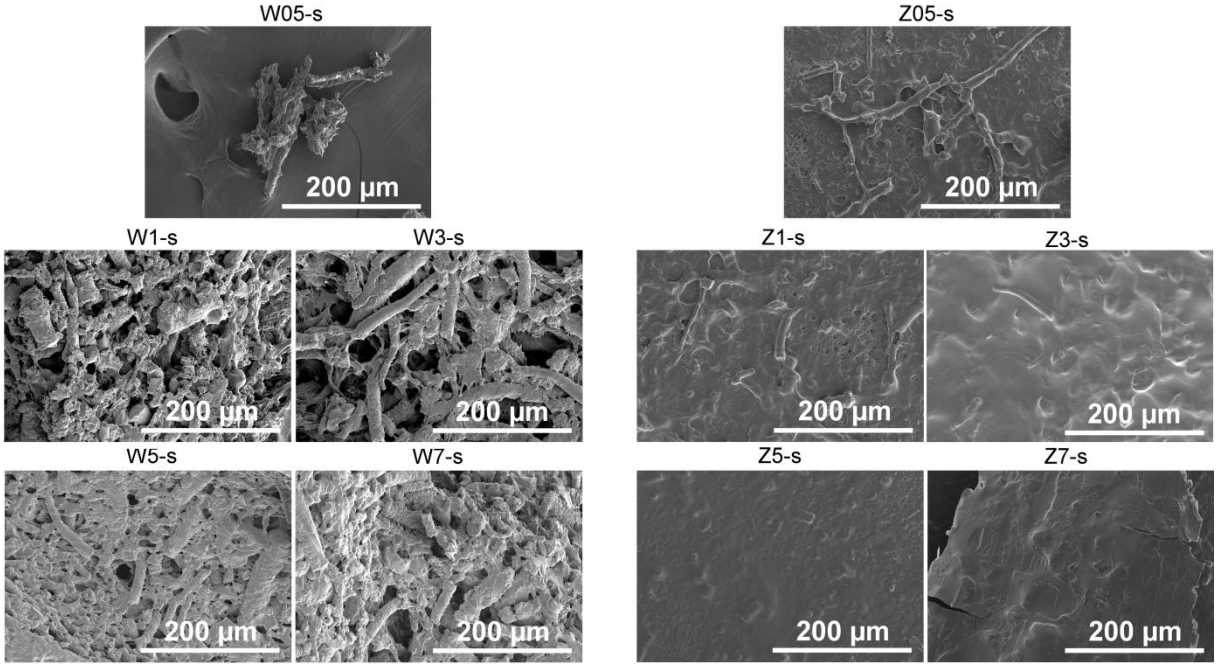

Figure 10 *SEM micrographs of solid DAC phase during solubilization at initial pH 3.5 (left) and 7.5 (right).*

Disregarding this molecular weight determining step, obtained solubilized DAC retained its characteristic features, namely content of reactive aldehyde

groups. These reactive substituents present on the polymer chain enable DAC utilization in the crosslinking applications for hydroxyl group containing polymers and thus can be further considered as an alternative to common used aldehyde-based low molecular crosslinkers. One of the main benefits of DAC as a crosslinker lies in its bio-macromolecular character, which makes it less toxic in comparison to its low molecular counterparts.

Next, the aging of DAC solution was studied in the terms of its functional group content and thermal stability (see Figure 11) and molecular weight distribution (see Table 6). In should be noted, that the slight discrepancy in measured DAC molecular weight between identically prepared samples Y7-f in solubilization study and fresh (1 day old) sample investigated in the DAC aging study was most likely caused by different GPC instrumentation used for these studies.

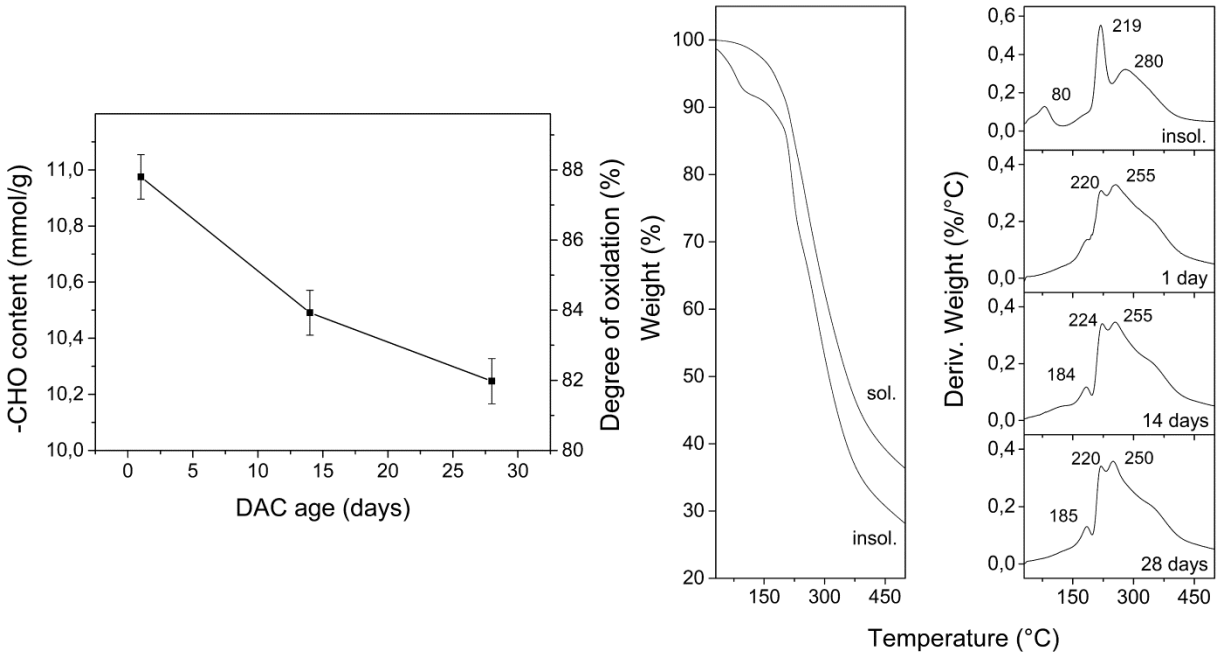

Figure 11 *Reactive aldehyde group content and degree of oxidation of prepared solubilized DAC estimated over period of 28 days of DAC aging (left). Thermogravimetric curves recorded for insolubilized DAC sample and aged solubilized-dried DAC samples (right). The lines connecting points in the left graph are only guides for eyes. [47]*

Due to known DAC sensitivity towards alkalic environment, the DAC solution was kept under acidic condition in current study. The low pH presumably suppresses the degradation processes described as β-elimination and further preserves the reactive aldehyde group content in time of DAC aging (see Figure 11 left part). The indirect alkalimetric titration showed less than a half decrease of reactive aldehyde content after four compared to previous studies on this topic [44].

Table 6 *GPC recorded data for DAC solutions in different aging time, where $\bar{M}_n$ is the number average molecular weight; $\bar{M}_w$ is the weight (mass) average molecular weight, M_p is the peak molecular weight, $\bar{M}_z$ is the third moment of molecular weight and PDI is the index of polydispersity ($\bar{M}_w$/ $\bar{M}_n$). [47]*

Time (days)	$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)	M_p (g/mol)	$\bar{M}_z$ (g/mol)	PDI (-)
1	2 600	6 100	5 500	10 200	2.36
14	3 100	7 400	7 000	12 000	2.38
28	2 000	6 900	6 700	13 200	3.46

The results form GPC were correlated with those of NMR and LC-MS study and further interpreted as several characteristic processes taking place during DAC aging. The results of these processes are also partially reflected in the change of thermal stability. The first process occurs immediately after DAC preparation and comprises of internal stabilization by the formation of intramolecular DAC hemiacetals mostly represented by two conformational isomers of DAC form **D** (marked as **D I** and **D II** in Figure 12) and form **C** (see Figure 4).

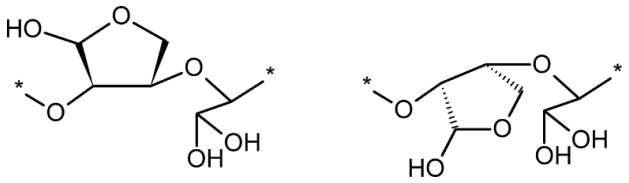

Figure 12 *Suggested structures of D I and D II conformers of DAC form D. [47]*

The second process was noticed after 14 days after DAC preparation and is manifested by reactions between DAC macromolecules resulting in the formation of intermolecular hemiacetals, structurally derived form DAC form **G** or **F**. This recombination process is reflected in the increased values of all momentums of molecular weight estimated by GPC. The third process, DAC chain fragmentation, becomes dominant with increasing time of DAC aging and results in the presence of low-temperature peak in weight loss rate (see Figure 11 right part). The significant increase in PDI and decrease in values of certain momentums of molecular weight ($\bar{M}_n$, $\bar{M}_w$ and M_p) testifies presence of such process in 28 days old solutions. However, low pH of the solution suppresses this fragmentation process (β-elimination) for the first 14 days of DAC aging. Hence, the evolution and accumulation of smaller DAC fragments evolution and accumulation is apparent after 28 days.

It should be stressed out, that the composition of fresh acidic DAC solution was investigated by NMR and the main forms of solubilized DAC identified for the first time. As the aging of DAC proceeded, no new NMR signals were

detected. The only observable changes were in the population of particular DAC forms. This observation can be assigned to the low pH conditions which increased the stability of the system in comparison with previous investigations reported by other authors.

It is also important to mention, that the processes of recombination and fragmentation run concurrently during entire solubilized acidic DAC aging timeframe. This fact is supported by the changes in the PDI values as well as in the monotonous increase of $\overline{M}_z$ values during DAC aging. The practical outcome of the investigation on the structural arrangements and properties of solubilized acidic DAC solutions during its shelf-life is the promising potential to be conveniently utilized for various purposes (such as crosslinking agent or intermediate in the preparation of other derivatives) without the need to prepare fresh DAC every time as it retains its functional properties at least for 28 days from its preparation.

(iii) The suitability of solubilized acidic DAC as a crosslinking agent for PVA was investigated along the utilization of different catalyst systems. The effects of catalyst systems based on the sulfuric or hydrochloric acid and the role of the age of pH-stabilized DAC solution on resulting properties of PVA crosslinked hydrogels were studied. Furthermore, the comparative crosslinking study of PVA utilizing DAC or GA crosslinkers in broad range of concentrations under equivalent conditions was conducted. The results of this study were expressed and compared in the terms of network parameters of prepared hydrogels. [43]

The applicability of the acidic DAC solution as a crosslinking agent for PVA was confirmed even after 28 days from its preparation. Moreover, DAC was found to be effective crosslinker with both chosen catalyst systems. It was revealed, that the properties of prepared PVA/DAC hydrogels are governed by the molecular weight of solubilized acidic DAC and selected catalyst rather than by the reactive aldehyde content. The functional DAC groups content responsible for the formation of crosslinks in PVA matrix decreases linearly in the course of 4 weeks (see upper left part of Figure 13). Thus the resulting properties of prepared hydrogels, such as swelling capacity, should exhibit linearly increasing trend as the crosslinking agent becomes less efficient over time. However, this was not observed. Instead, the trends of hydrogel properties correlate with the evolution of DAC molecular weight. There is about 20 % increase in its $\overline{M}_n$ after 14 days caused by intermolecular hemiacetal formation (DAC recombination) followed by decrease of this quality about 40 % after 28 days from crosslinker preparation (DAC fragmentation), see top curve in upper right graph in Figure 13. [43, 47]

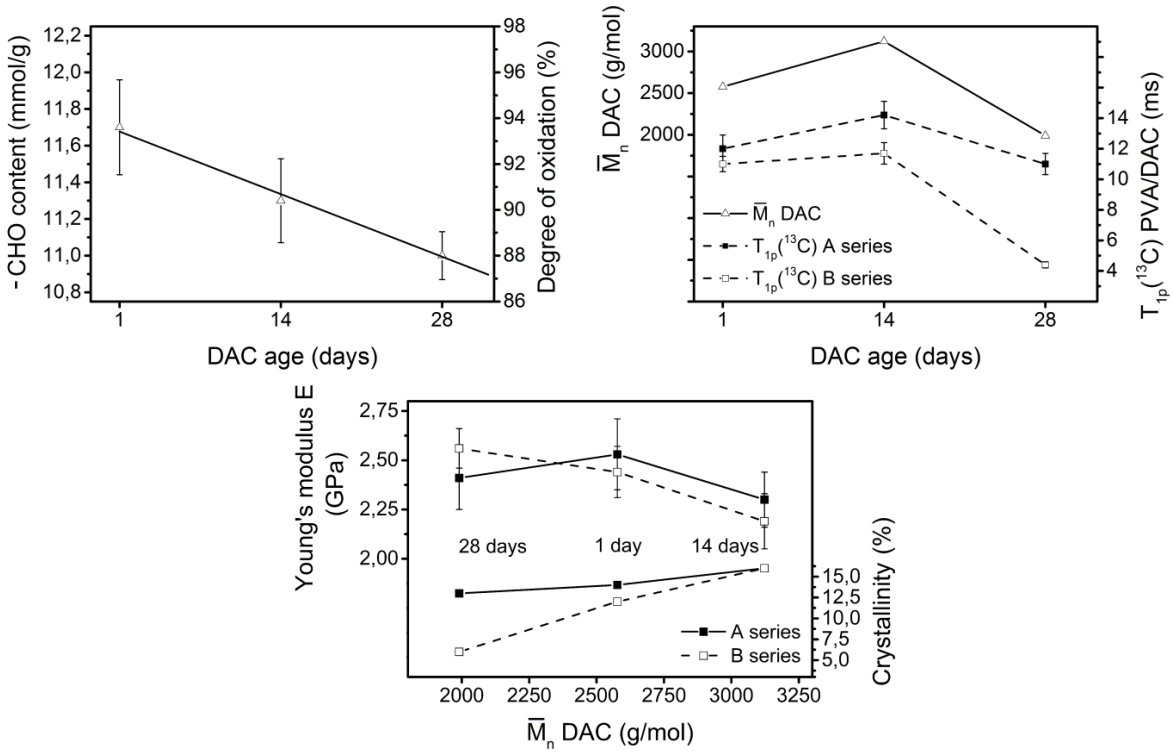

Figure 13 *Decrease of reactive aldehyde group with DAC aging (top left); correlation between $\overline{M}_n$ of DAC in solutions of various age (Münster et al., 2017) and $T_{1\rho}(^{13}C)$ values of resulting PVA/DAC hydrogels (top right); correlation between $\overline{M}_n$ of DAC and Young's modulus and crystallinity of PVA/DAC xerogels prepared using different catalyst system (A and B series) with marked age of used DAC crosslinker (bottom center). The lines connecting points in the graphs are only guides for eyes. [43, 47]*

Similar trends were observed in number of measured properties of prepared PVA/DAC xerogels and hydrogels such as polymeric domain flexibility parameter $T_{1\rho}(^{13}C)$ estimated by solid-state NMR (see two dash-lined curves in upper right graph in Figure 13) and the set of network parameters, see Figure 14. Moreover, the lower graph in Figure 13 depicts dependence of Young's modulus and crystallinity on $\overline{M}_n$ of DAC and documents the influence of DAC crosslinker's molecular weight on bulk properties such as stiffness and percentage of crystalline phase in xerogels. Schematic structural models representing the two extreme situations in PVA/DAC xerogels, i.e. samples B02 and B03 is given in Figure 15. The sample B02 was crosslinked by smaller number of larger DAC macromolecules present in 14 days old DAC solution and exhibits the largest crystallinity. Therefore, this sample contains most likely regions comprised of larger PVA crystallites developed within the sparsely crosslinked polymer network with highest polymeric domain flexibility. On the other hand, the sample B03 was crosslinked by larger number of smaller DAC molecular fragments present it the oldest DAC solution. Hence, the sample B03 has more rigid and densely crosslinked polymer network containing less evolved PVA crystallites.

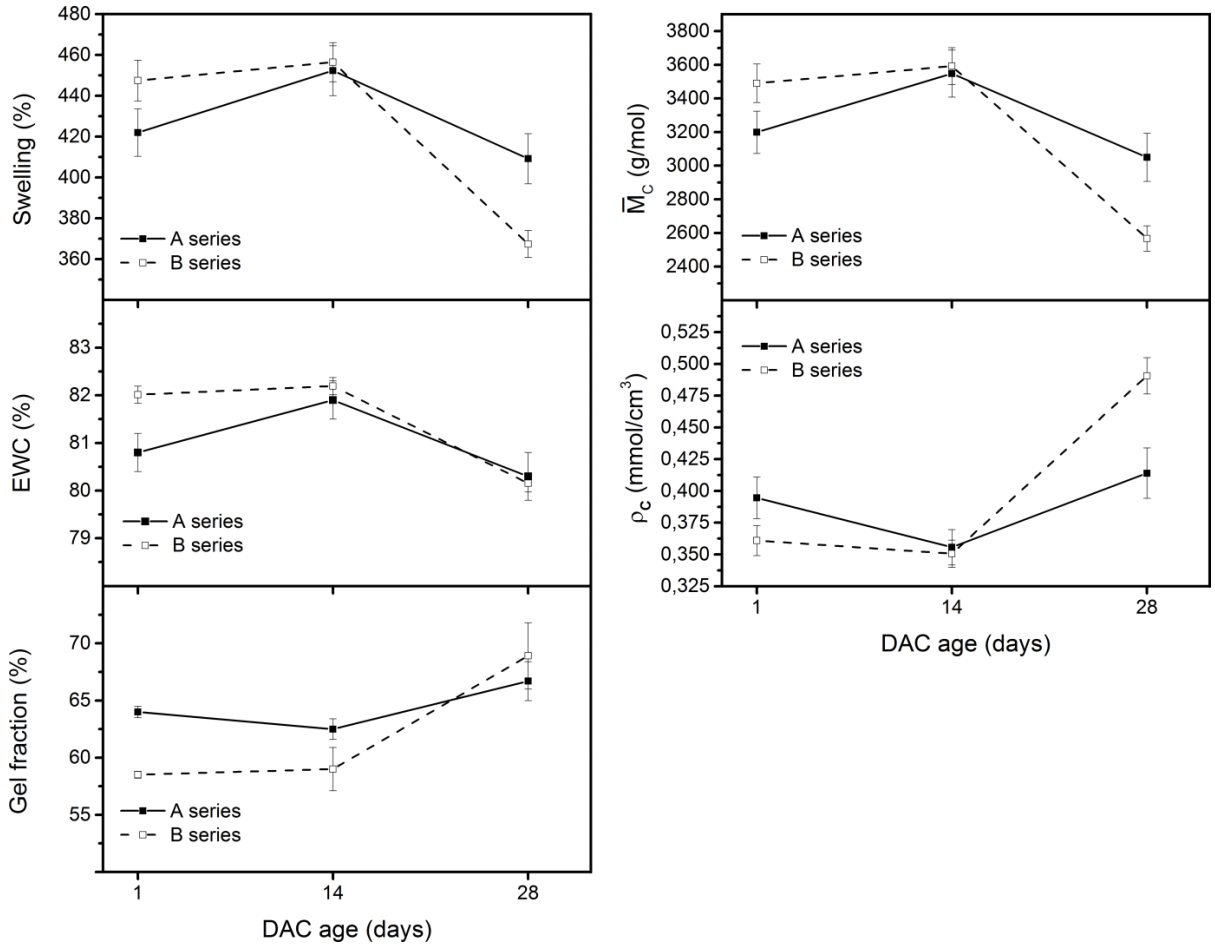

Figure 14 *Influence of DAC age used for crosslinking on the network parameters of prepared PVA/DAC hydrogels. The graphs show percentage of swelling, equilibrium water content (EWC), gel fraction, average molecular weight between crosslinks ($\bar{M}_c$) and crosslink density (ρ_c) of both prepared series of PVA/DAC samples crosslinked by fresh and aged DAC. The graph lines connecting points are only guides for eyes. [43]*

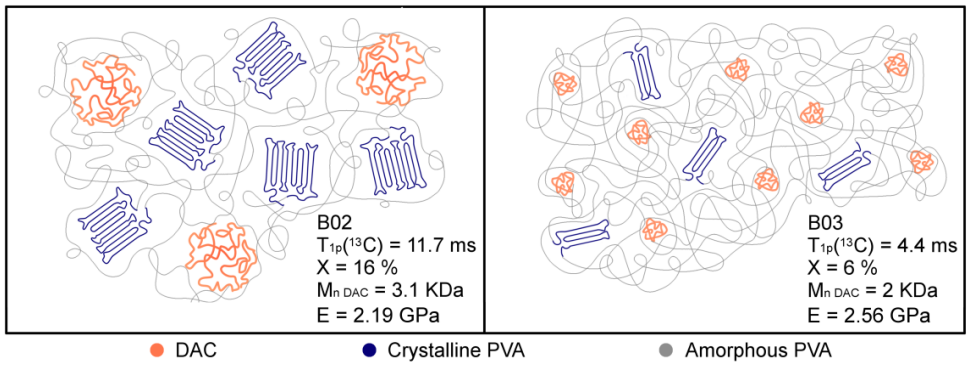

Figure 15 *Schematic representation of the structure of the respective xerogels with their relation between flexibility ($T_{1\rho}(^{13}C)$), crystallinity (X), Young's modulus (E) and number average molecular weight ($\bar{M}_n$) of DAC. The orange coils correspond to ($\bar{M}_n$) of DAC, the arrays of blue lines represent polymer chain crystallites, and the grey lines represent the amorphous phase of the polymer with physical entanglements. The size, ratio, and number of depicted features is intentionally exaggerated. [43]*

The properties of PVA/DAC hydrogels prepared using fresh/aged DAC show similar quantitative trends when different catalyst systems employed (see Figure 16). However, there are noticeable differences in material properties of hydrogels prepared using the oldest, most fractioned DAC and different catalyst. Based on the data obtained from NMR, tensile testing and network parameters evaluation, sulfuric acid accompanied by methanol and acetic acid seem to be (a) more efficient catalyst or (b) may induce DAC degradation or (c) influence physical PVA entanglements. These possibilities result in the formation of PVA hydrogel with increased crosslink density and other related network parameters. The downside of the utilization of this catalyst system lies in non-linear behaviour of several correlated properties arising from the complexity of this specific catalyst system. Comparatively, the utilization of fairly simple catalyst based on diluted hydrochloric acid produces PVA hydrogels of predicable, structurally stable and less DAC molecular weight-dependent properties.

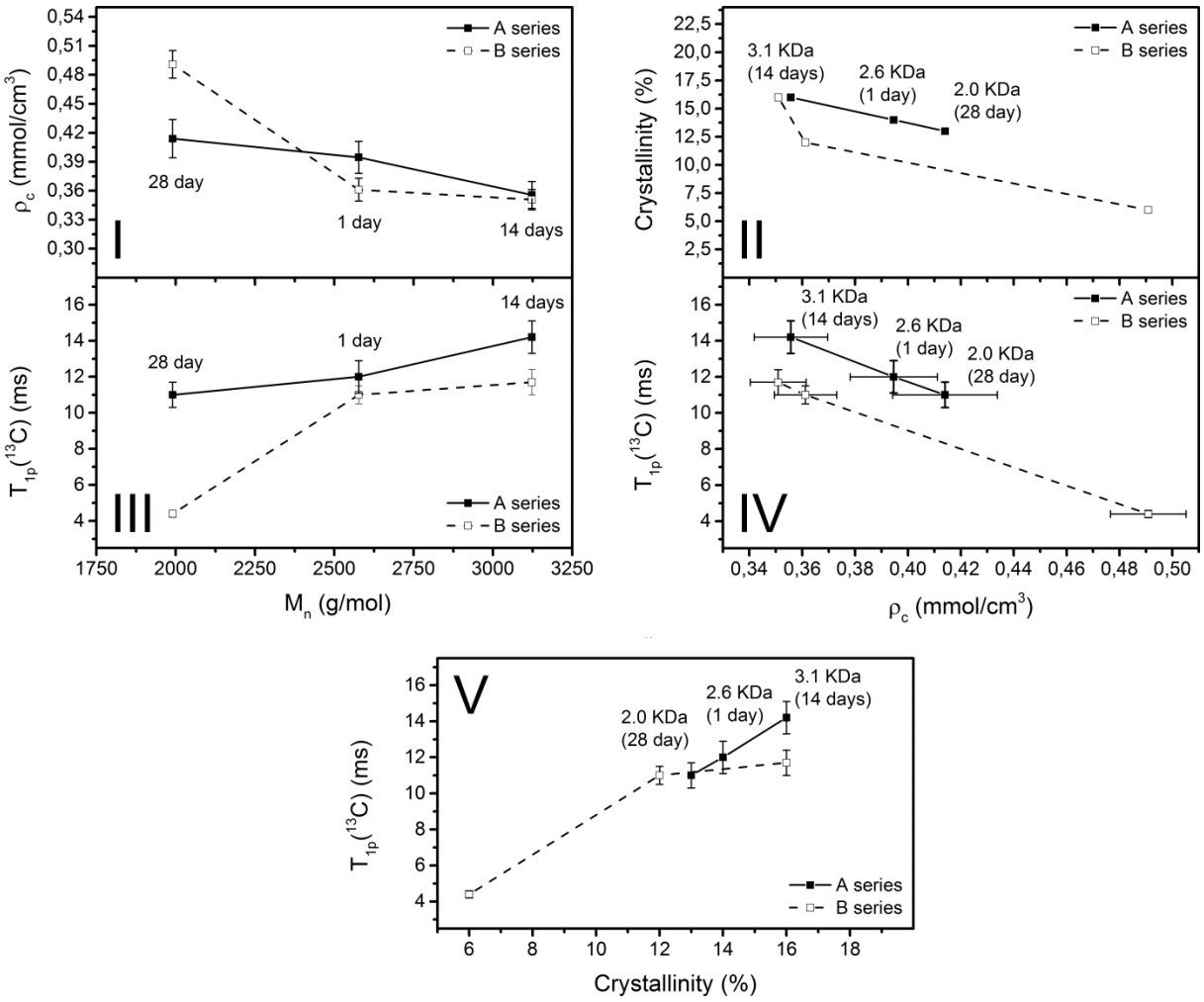

Figure 16 *Correlation between data measured by various methods for PVA/DAC prepared using aged DAC and different catalyst system. The lines connecting points in the graphs are only guides for eyes. The data points are labelled by corresponding age and number average molecular weight for one series (A) only in each graph. The second series (B) has the same order of data points from left to right always. [43]*

The fact, that crosslinkers molecular weight and choice of catalyst are the key factors in hydrogel preparation implies potential possibility of "tuning" of hydrogel properties without need for other additives.

The last part or this research was devoted to the comparison of macromolecular DAC to low molecular GA crosslinker. The exceptional crosslinking efficiency of DAC at very low concentrations outperforms GA and enables to form hydrogels with extreme swelling capacity (see Figure 17).

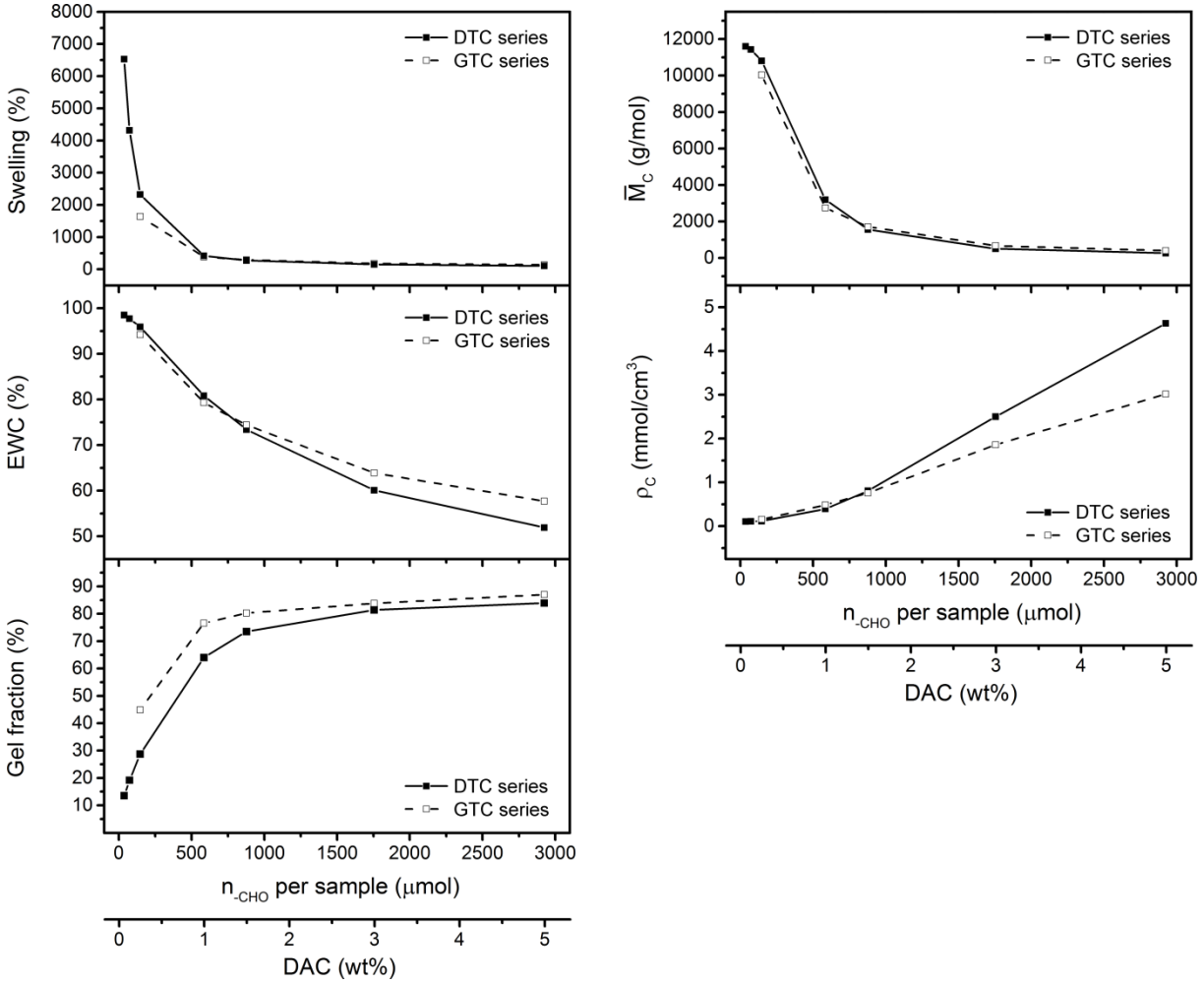

Figure 17 *The results from comparative crosslinking study showing dependence of PVA/DAC (DTC) and PVA/GA (GTC) hydrogels network parameters on the used DAC or GA crosslinker amount defined by chemical amount of reactive aldehyde groups per sample and "Mowiflex" type of PVA. The equivalency between DAC and GA reactive group concentrations is expressed by the two bottom x-axes. The lines connecting points in the graphs are only guides for eyes. [43]*

Such crosslinking capability of DAC can be explained as a result of its macromolecular character, which forms "two-phase" crosslink network topology composed of regions with high crosslink density adjacent to the DAC

macromolecule embedded in a chemically uncrosslinked matrix comprised of sizable sections of free PVA chains, which are physically entangled only (see Figure 18).

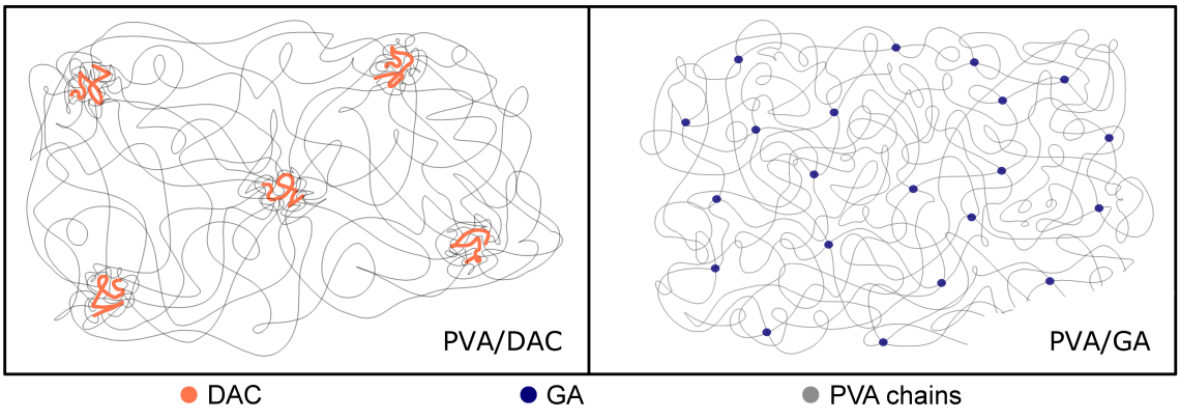

Figure 18 *Network topology of PVA/DAC is shown in the left part. It is composed of (i) regions containing high local crosslink density adjacent to DAC macromolecules (orange) embedded in (ii) larger regions comprised of free, chemically unbound, PVA chains (grey) which can be only physically entangled. Some of these chains link the regions (i) together. The right part of the figure shows the homogeneous network topology of PVA/GA crosslinked by GA (blue). The size, ratio, and number of depicted features is intentionally exaggerated for better understanding. [43]*

Some of these chains linking the densely crosslinked regions together are responsible for the preservation of PVA hydrogel integrity. Other chains can be joined to one densely crosslinked region only. A single PVA chain may be attached to one DAC macromolecule more than on one site forming thus circles hypothetically allowing concatenation. Relatively sparse distribution separation of high-density crosslink regions results is responsible for the large swelling ability of DAC/PVA hydrogels. On the other side of the crosslinker concentration range, DAC enables formation of highly crosslinked hydrogels of comparable of even better material characteristics that those obtained by utilizing GA. Furthermore, due to presumably lower toxicity of DAC compared to GA, this cellulose derivative is promising compound for the application in medicine and pharmacy.

8. SUMMARY OF CONTRIBUTIONS TO SCIENCE AND PRAXIS

The main contributions of this research to science and praxis include following achievements (i) preparation and characterization of solubilized dialdehyde cellulose (DAC) and its use as a poly(vinyl alcohol) (PVA) crosslinker, (ii) investigation of the solubilization effects on the properties of DAC (iii) analysis of DAC structure in acidic media during its aging, (iv) utilization of fresh/aged solubilized DAC as a PVA crosslinker with evaluation of its crosslinking abilities and finally (v) comparison of network parameters of PVA hydrogels prepared using DAC and glutaraldehyde (GA) crosslinker in wide range of concentrations.

Periodate oxidation does not influence molecular weight. However, subsequent solubilization was proven to cause severe degradation of resulting solubilized DAC.

Significant improvement of DAC stability in comparison to the previous studies and thus prolongation of its shelf-life and applicability was achieved via our originally developed low pH procedure. DAC is initially stabilized by intramolecular and subsequently intermolecular hemiacetal formation as confirmed by NMR and GPC. Fragmentation occurs during observed DAC aging as well as minor decrease in reactive aldehyde group content.

It was found that DAC molecular weight influences the properties of PVA/DAC hydrogels more than its reactive aldehyde group content. The changes in molecular weight or functional group content did not compromise DAC crosslinking ability even 28 days from its preparation.

It was demonstrated that solubilized and stabilized DAC exceeds crosslinking efficiency of GA at very low concentrations. Moreover, it forms denser network at high concentrations and principally different network topology compared to GA. This enables to prepare hydrogels with wide range of properties. Furthermore, arising from its macromolecular character, it is considerably less toxic than low molecular crosslinkers. Preliminary results confirmed low toxicity and biocompatibility of PVA/DAC hydrogels. Future work will focus on hydrogels loading with active compounds such as platinum based complexes, their subsequent release kinetic and biological testing.

Besides DAC utilization as crosslinker, it can serve as an intermediate in the preparation of dicarboxy cellulose (DCC) which is another promising drug carrier. Our recent study showed DCC high loading efficiency (90 %) and capacity (60 % w/w) of platinum based anticancer drugs. Furthermore, it allows adjustable and pH sensitive drug-release kinetics.

To generalize, the results embodied in this Thesis open a new field for applications of DAC and its derivatives, namely in medical sector and pharmacy as promised by ongoing research.

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LIST OF ABBREVIATIONS

Alphabetically ordered

AGU	D-anhydroglucopyranose unit
CNWs	Cellulose nanowhiskers
CP/MAS	Cross-polarization/magic-angle-spinning
DAC	Dialdehyde cellulose
DCC	Dicarboxy cellulose
EWC	Equilibrium water content
FT-IR	Fourier-transform infrared spectroscopy
GA	Glutaraldehyde
GPC	Gel permeation chromatography
IR	Infrared
LC-MS	Liquid chromatography–mass spectrometry
NMR	Nuclear magnetic resonance
PVA	Poly(vinyl alcohol)
PVA/DAC	Poly(vinyl alcohol) hydrogels crosslinked by dialdehyde cellulose
PVA/GA	Poly(vinyl alcohol) hydrogels crosslinked by glutaraldehyde
SEM	Scanning electron microscopy
sol.	Solubilization/solubilized
temp.	Temperature
TGA	Thermogravimetric analysis
WoS	Web of Science
XRD	X-ray diffraction analysis
α-cell.	Alpha cellulose

LIST OF SYMBOLS

Alphabetically ordered

C2, C3, C6	Numbered carbon atoms of D-anhydroglucopyranose unit
E	Young's modulus
M	Molarity (molar concentration)
$\bar{M}_c$	Average molecular weight between crosslinks
$\bar{M}_n$	Number average molecular weight
M_p	Peak molecular weight
$\bar{M}_w$	Weight (mass) average molecular weight
$\bar{M}_z$	Z-average (third moment) of molecular weight
$n_{\text{-}CHO}$	Chemical amount of crosslinkers reactive aldehyde groups
PDI	Index of polydispersity
pH	Potential of hydrogen
$T_{1\rho}(^{13}C)$	Carbon spin-lattice relaxation time in rotating frame
vol%	Percentage by volume
wt%	Percentage by weight
X	Crystallinity
ρ_c	Crosslink density

LIST OF UNITS

Alphabetically ordered

%/°C	weight percentage per degree Celsius
°C	degree Celsius
cm^{-1}	reciprocal centimetre
g/mol	gram per mole
GPa	gigapascal
h	hour
kDa	kilodalton
mg/mL	milligram per millilitre
mL	millilitre
mmol	millimole
$mmol/cm^3$	millimole per cubic centimetre
mmol/g	millimole per gram
ms	millisecond
µm	micrometre
µmol	micromole

LIST OF PUBLICATIONS

Journal articles relevant to the Doctoral Thesis:

[1] MÜNSTER, L., VÍCHA, J., KLOFÁČ, J., MASAŘ, M., KUCHARCZYK, P. and KUŘITKA, I. Stability and aging of solubilized dialdehyde cellulose. *Cellulose*. 2017. Vol. 24, no. 7, p. 2753–2766. DOI 10.1007/s10570-017-1314-x.

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[1] MÜNSTER, L. and KUŘITKA, I. Vliv koncentrace katalyzačního systému a teploty sušení na síťování PVA/DAC směsi. In : *PLASTKO 2016*. Zlín, 2016. p. 507–515. ISBN 978-80-7454-590-0.

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