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CHEMICAL RECYCLING OF WASTEPAPER TO VALUABLE PRODUCTS

BY

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Abstract. The aim of the present study was to develop a method for preparing cellulose-based hydrogels (HGs) from waste paper (WP). Newsprint paper and various types of cardboard were subjected to pretreatments and then dissolved in DMAc/LiCl. Stable hydrogels were formed by spontaneous gelation from the solutions of WP. The properties of the HGs were examined both chemically and by FTIR, WAXS and SEM. FTIR confirmed the chemical purity of HGs. The structure of initial samples, HGs and freeze-dried HGs was characterised with WAXS. The cellulose I structure in the initial WP samples was totally disordered in solutions and partly recrystallized to the structure of cellulose II in freeze-dried HGs. According to SEM, the HGs revealed a random network with evenly distributed through pores of different sizes.

Keywords: waste paper; dissolution; hydrogels; structure; morphology.

1. Introduction

One of the goals of sustainable development strategy claimed by United Nations is to ensure sustainable consumption and production (17 Sustainable Development Goals). Management of unhazardous solid wastes is the subject of

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Chapter 21 of Agenda 21 (Agenda 21, 1992). The priorities of reuse and recycling of solid wastes along with waste prevention and minimization were given in that document in 1992 and those primary issues are still actual (*e.g.* Green Deal, Circular Economy Action plan in EU). With the rapid growth of population, even more rapidly the amount of waste of production and consumption is increasing. That is why the new approaches for waste management are needed.

The proportion of paper and board is about one-third of the total amount of waste. Waste paper is probably one of the most collected fractions of waste. Collection and recycling of WP is a profitable business with billion euros involved. Conventionally, WP that was collected from enterprises and individuals goes to the papermaking process again and it closes the paper life cycle. However, it is possible to recycle WP only a certain number of times and every time the quality of the product become lower. Due to this, there is a large number of WP, for instance, waste newspapers and board, which are the low-grade paper products (LGP), that have little or no value in papermaking.

Even paper or board with the lowest quality still consists of cellulose fibres which are valuable raw material with unique properties. There are a number of products where the waste LGP is used. Namely, the recycled LGP shows great adsorption capacity for dyes and other water contaminants (Okada *et al.*, 2003; Islam *et al*., 2019); LGP along with others fillers is added in cement composites (Hospodarova *et al.*, 2018); LGP may be converted to bioethanol (Wang *et al*., 2012; Wang *et al*., 2013) and sugars (Walpot, 1986), or applied for preparing natural fibre composites with other polymers (Zhang W. *et al*., 2019). Thus, cellulose fibres may be extracted from WP and successfully utilized further in the same way as ordinary cellulose.

One of the most recent directions in paper recycling is extracting of nanocellulose from WP. In few studies, it was shown that acid hydrolysis with preliminary treatment steps led to obtaining of nanocellulose (Danial *et al*., 2015; Campano *et al*., 2017; Mikhailidi *et al.*, 2019). Concentrated sulphuric acid was applied for hydrolysis, while bleaching and mercerisation were the common pretreatments. The drawback of this method was that high concentrations of chemicals were used, that was harmful for the environment.

Another pathway to utilization of cellulose fibres reused from LGP is the dissolution following by the regeneration to cellulose products with different shapes including hydrogels and aerogels. Very few articles are available on this topic (Zhang *et al.*, 2019; Fridrihsone *et al.*, 2019). Recently, we have described the preparation of the super-swollen hydrogels from hardwood pulp, flax fibers and cotton cellulose regenerated from the solutions of DMAc/LiCl (Kotelnikova *et al.*, 2016). The aim of this study was to develop an effective and low-cost method for preparing cellulose-based functional hydrogels directly from the paper wastes. Characterization of the properties of the HGs was the second goal of this study.

2. Preparation of Hydrogels from Low-Grade Waste Paper

Two grades of low-quality waste paper were used: newsprint (NP) and various types of cardboard (CB), such as packaging CB and filter CB, all the samples were de-inked. Experimental flow chart is schematically shown in Fig. 1. Firstly, the samples were subjected to mechano-chemical defibration with hot water under stirring and subsequent grinding. Then prepared fibre samples were activated with a solvent exchange, as follows: water – ethanol – DMAc. After pretreatment, samples were dissolved in the solution of DMAc/LiCl (LiCl concentration 8 wt.%) at 30ºC or 70ºC, according to the methods described elsewhere (Kotelnikova *et al.*, 2016).

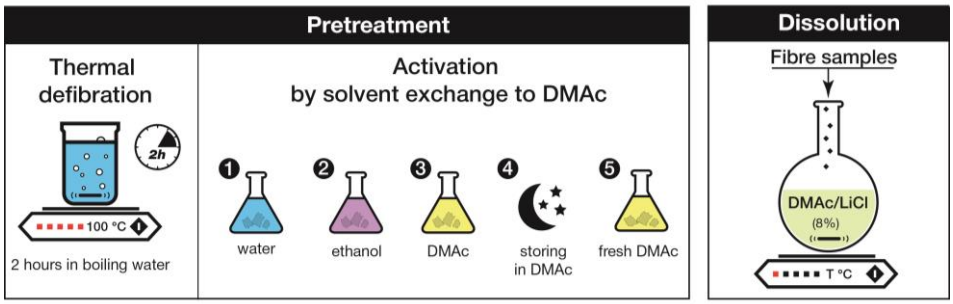

Fig. 1 – Experimental flow chart.

An important issue of our study was to find routes to regenerate samples from solutions with formation of the HGs. Once the fibres were partly dissolved, the solutions were separated from the undissolved part and poured into special forms. Formation of the gels from the solutions occurred at the ambient atmosphere and temperature and without any non-solvents, when slow aggregation was accompanied by a spontaneous gelation. The super-swollen HGs were formed by the replacement of the solvent DMAc/LiCl to water. The solutions and HGs were mainly coloured from yellow to brown. The transparency of HGs varied also from totally transparent to cloudy or opaque. Nevertheless, they could be used as prepared. For further study, the HGs were freeze-dried. Digital images of solution, hydrogel and freeze-dried hydrogel (FDHG) obtained from packaging CB are shown in the Fig. 2 as an example. Physico-chemical methods were applied to characterize the initial samples and obtained products.

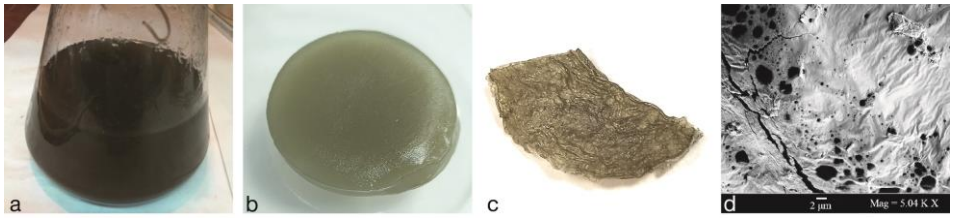

Fig. 2 – Digital images of the samples obtained from packaging CB: *a* – solution, *b* – hydrogel, *c* – freeze-dried hydrogel; *d* – SEM image of freeze-dried hydrogel.

3. Characterization of the Properties of Hydrogels Compared to these of the Starting Samples

WAXS was used to characterize the structure of the samples, FTIR was applied to prove the chemical composition of the HGs, and SEM was employed to study the surface morphology.

Concentration of the waste paper in the solutions was from 0.3 to 1.0 wt. %. Solubility (Sol) of the WP samples in DMAc/LiCl mainly depended on the type of the sample and the additional grinding during the pretreatment.

The Sol varied in a wide range, namely, from 21 to 99 wt.% (Table 1). CB samples demonstrated higher Sol than NP ones. This was apparently due to difference of surface and internal morphology of the samples. Thus, the morphological structure of the filter cardboard with the highest Sol (99 wt.%) was characterized by looseness and, accordingly, good permeability. Samples of the packaging CB with glued layers exhibited an increased stiffness and density. Due to this, they had a fine-pored structure and lower permeability. Therefore, the solubility of the sample of CB was two times lower than that of the filter board. The solubility of NP distinguished from CB both because of the difference in the morphological structure of the starting material and the method of dissolution and additional grinding. For these reasons, Sol of NP samples was significantly lower than this of CB samples.

Equilibrium water content (EWC) and porosity were very high for the samples of HGs. Some of the EWC values were higher than these for the HGs obtained from the samples of powder celluloses (Kotelnikova *et al.*, 2017). The porosity values of the hydrogels ranged from 97.08 to 98.87%, which matched the values obtained for the powder cellulose. Thus, the obtained hydrogels were the superswollen and porous samples.

According to the FTIR analysis, both initial NP and CB had absorption bands characteristic to cellulose I and revealed a high content of cellulose. However, they contained lignin and hemicelluloses in negligible amounts. The spectra of the HGs revealed a higher chemical purity and a sharper resolution of absorption bands. The overall spectra of the regenerated samples corresponded

largely to the cellulose I polymorph. However, this non-trivial result requires further research.

Table 1
Solubility of the Waste Paper in DMAc/LiCl and Characteristics of the Obtained Hydrogels

Sample	Initial material	Solubility, %	Equilibrium water content, %	Porosity, %
1	Packaging cardboard	50	2913	98.26
2	Filter cardboard	99	1646	-
3	Newsprint	21	3717	98.87
4	Newsprint	25	1435	97.08
5*	Flax powder cellulose	99.5	2500	98.90

*Characteristics of hydrogels obtained from flax powder cellulose are given for comparison (Kotelnikova *et al.*, 2017).

The structure of the initial samples, the HGs and FDHGs was studied with WAXS method. The X-ray crystallinity of the pristine CB samples (Cryst. = 33.2%) was higher than that of the NP (Cryst. = 22.6%). All crystallinity values were calculated using Amorphous fitting method (Karim Saurov *et al*., 2019).

One of the examples of the X-ray patterns for the sample prepared from CB is shown in Fig. 3. The pattern of initial CB revealed reflections characteristic of the cellulose I crystal structure (Fig. 3, a). The pattern of the HG did not contain any reflections of cellulose lattice and resembled the diffraction pattern of water (Fig. 3, b). The pattern of the FDHG revealed the structure of partially ordered cellulose II. So, the structure of the pristine sample transformed from cellulose I to the partly ordered cellulose II in the freeze-dried sample. Herewith, the structure of the intermediate HG was completely disordered.

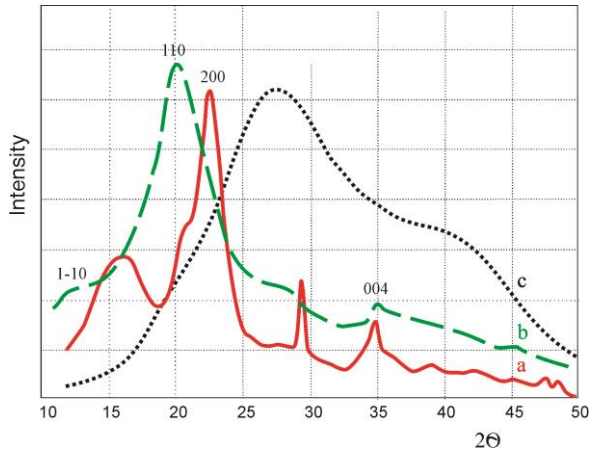

Fig. 3 – X-ray patterns of the pristine CB sample (a), hydrogel (b) and freeze-dried hydrogel (c).

The surface morphology of the initial samples and FDHGs was studied using SEM. The surface of the initial samples of NP and CB had a loosely packed structure with a partial orientation of the fibres. On the surface of fibres and in the near-surface layers, elements of a porous structure were rare.

Both FDHGs obtained from NP and CB had a completely disordered structure, however, with a well-developed porous system. The surface of the FDHG from CB (Fig. 2*d*) revealed a large number of through pores which penetrated the entire volume of the sample and differed significantly in size. The pores in FDHGs were much smaller than in the initial samples, while the pore size of the FDHG-NP (250-450 nm) was generally smaller than the pore size of the GDHG-CB (30-4000 nm).

Evidently, it's the porosity that should largely determine the high sorption properties of the HGs. The sorption capacity of the swollen and freeze-dried hydrogels was studied in relation to the direct dye Methylene blue. The swollen hydrogels had low apparent sorption capacity, *i.e.* in the range 1-2 mg/g for both hydrogels, while the freeze-dried samples exhibited significantly higher sorption capacity ranged from 28 to 32 mg/g.

4. Conclusions

1. An efficient and low-cost method of obtaining hydrogels from waste paper and cardboard was developed for the first time.

2. The dissolution of wastepaper in DMAc/LiCl was studied and facile regeneration procedure to prepare the hydrogels from the solutions was elaborated.

3. The HGs had the high equilibrium water content values and the porous structure.

4. According to FTIR spectroscopy, the functional composition of the regenerated HGs corresponded to cellulose of high chemical purity.

5. The crystal structure of the initial wastepaper samples corresponded to cellulose polymorph I, while the structure of the freeze-dried HGs corresponded to a partially ordered cellulose polymorph II.

6. According to SEM, the freeze-dried HGs had a system of randomly distributed pores of different sizes, which determined their high sorption capacity.

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⁎*⁎ *17 Sustainable Development Goals*, Department of Economic and Social Affairs, UN, URL: https://sdgs.un.org/goals/goal12.

⁎*⁎ *Agenda 21*, United Nations Sustainable Development, United Nations Conference on Environment & Development, Rio de Janerio, Brazil, 3-14 June 1992, URL: https://sustainabledevelopment.un.org/content/documents/Agenda21.pdf.

RECICLAREA CHIMICĂ A DEȘEURILOR LA PRODUSE VALOROASE

(Rezumat)

Scopul prezentului studiu a fost de a dezvolta o metodă de preparare a hidrogelurilor pe bază de celuloză (HG) din deșeuri de hârtie (WP). Hârtia provenită din ziare și diferite tipuri de carton a fost supusă pretratărilor și apoi dizolvată în DMAc / LiCl. Hidrogelurile stabile s-au format prin gelificarea spontană din soluțiile de WP. Proprietățile HG-urilor au fost examinate atât chimic, cât și prin FTIR, WAXS și SEM. FTIR a confirmat puritatea chimică a HG-urilor. Structura probelor inițiale, HG și HG liofilizate a fost caracterizată prin WAXS. Structura celulozei I din probele inițiale de WP a fost complet dezordonată în soluții și recristalizată parțial la structura celulozei II în HG liofilizate. Potrivit SEM, HG-urile au prezentat o rețea aleatorie, distribuită uniform prin pori de diferite dimensiuni.