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A NOVEL CLASS OF HYDROPHOBIC CELLULOSE MATERIALS: LIGHTWEIGHT XEROCELLULOSE

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INTRODUCTION

Nowadays the urge to find and create new alternatives for sustainable utilisation and use of renewable materials is greater than ever. In view of these circumstances cellulose, as renewable resource, is considered a promising material which could help to provide a possible solution for this quest we are facing momentarily. The development of novel cellulosic materials with high added value is thus of great interest.

Aerocellulose, an aerogel-like highly porous and ultra-light cellulose, is a new material recently developed in our laboratory^{1,2}. Aerocellulose density is around 0.05-0.2 g/cm³, with pore sizes varying from a few nanometres to a few microns and rather high specific surface of 200-300 m²/g. It is prepared via cellulose dissolution followed by coagulation and drying with supercritical CO₂. Drying under supercritical conditions is needed to minimize pore collapse and cellulose densification. Potential Aerocellulose applications can vary from biomedical, pharmaceutical and cosmetics to thermal insulation and electrochemical (when pyrolysed)³. However, for some applications cellulose hydrophilicity may cause serious problems. Additionally, the process of drying via supercritical CO₂, even if very efficient, is rather time consuming, necessitates quite huge investment and could also present difficulties in terms of large scale utilisation if, for example, some continuous production of monolithic materials is required.

Within this paper we are introducing a brand new form of highly porous cellulose, so-called Xerocellulose, made from hydrophobically modified cellulose. Associated fonctionnalization allows drying under ambient pressure at room temperature without sample high contraction and thus avoiding drying in supercritical conditions. Furthermore, due to hydrophobisation, we were also able to reduce water vapours adsorption capacity significantly. The route of cellulose ambient-dried preparation and the influence of cellulose concentration and of degree of substitution (DS) on Xerocellulose density, morphology and water adsorption capacity will be presented and discussed.

MATERIAL AND METHODS

For the modification of the cellulose we have chosen microcrystalline cellulose Avicel® purchased from Sigma Aldrich (France) and used it without further purification. Solvents N, N-dimethylacetamide (DMAc), methanol (MeOH) and dimethylformamide (DMF) used for the reaction were purchased from Fisher Scientific whereas the reagents tritylchloride and LiCl were from Acros Organics and used without further purification. The cellulose dried in an oven at 80°C and solvents were dried with molecular sieves (3Å) over three days prior to the synthesis.

Cellulose modification is schematically presented in Figure 1: tritylchloride reacted with OH groups of the polysaccharide according to ref.4. The reaction was performed in LiCl/N,N-Dimethylacetamide. The reaction mixture of Avicel®, solvent and tritylchloride was stirred for 48h at elevated temperatures. The obtained modified cellulose was then dissolved in DMF and coagulated in methanol, washed in methanol and dried by evaporation at 40°C under primary

vacuum. The most probable OH group which reacts with the tritylchloride is the hydroxyl group at carbon 6 of the anhydroglucose unit (Figure 1) because it is less sterically hindered in comparison with the other hydroxyl groups which enables the bulky tritylchloride to easily attack on this side. Additionally the choice of solvent is known to have an effect of the stereoselectivity⁴.

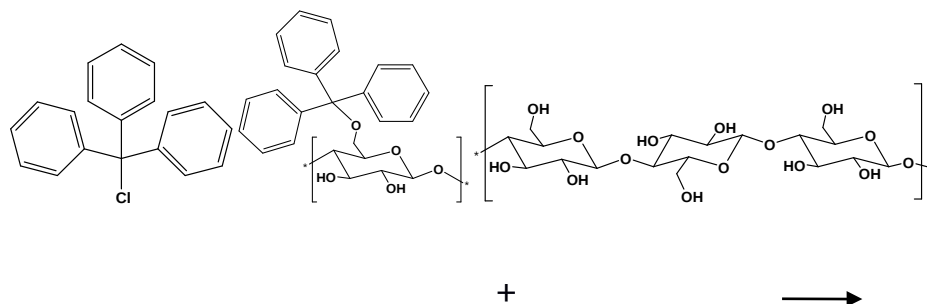


Figure 1: Reaction scheme of cellulose with tritylchloride according to ref.4

The Xerocellulose was prepared from dissolving modified cellulose in DMF, coagulation in the same anti-solvent (methanol) and further washing in ethanol. The samples were dried at room temperature under ambient conditions within two days.

IR spectroscopy was used to analyse the samples prepared in order to prove cellulose derivatisation. Xerocellulose morphology was studied by SEM (Zeiss supra 40 equipped with a Gemini® column). Apparent density was measured by accurately measuring sample dimensions and weight.

RESULTS

IR spectra of the initial (non-modified microcrystalline cellulose) and of two samples of modified cellulose with different degrees of substitution were performed. We could distinguish the spectra of the samples in respect to their different DS. The OH band decreased significantly and showed different intensity as well as new arising peaks for the aromatic functionalities appeared also varying in intensity due to different DS.

We obtained Xerocellulose samples with an increased hydrophobicity but at the same time maintaining low density properties like conventional Aerocellulose, within 0.2 – 0.3 g/cm³. Xerocellulose morphology was significantly different in comparison to conventional cellulose. The Aerocellulose structure was more a fibre-like structure whereas the tritylcellulose network was formed by bigger “rose-shape” subunits which form a continuous porous network but more fragile and less flexible.

Via SEM we could also observe the difference in morphology of the samples in respect to their DS. Xerocellulose density strongly depends on the degree of substitution.

CONCLUSIONS

Using cellulose hydrophobisation in homogeneous conditions, we obtained brand new ambient-dried and lightweight cellulose so-called Xerocelluloses. Xerocellulose was made via dissolution-coagulation and evaporative drying in ambient conditions. This approach opens promising ways in making novel high-added-value hydrophobic cellulosic aerogel-like materials. For future big-scale applications avoiding drying super critically with CO₂ this could present an interesting alternative of producing light-weight porous cellulose material via a continuous processing route.

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