ISGC 2019
May 13th - 17th

N°350 / OC
TOPIC(s) : Biomass conversion / Alternative solvents

Sustainable Cellulose Solubilization, Regeneration and Derivatization in a DBU-CO2 Switchable Solvent System

AUTHORS

KELECHUKWU ONWUKAMIKE / KIT, GERMANY. UBX, FRANCE, MATERIALWISSENSCHAFTLICHES ZENTRUM MZE, STRAßE AM FORUM 7, KARLSRUHE
ETIENNE GRAU / UNIVERSITY OF BORDEAUX, LABORATOIRE DE CHIMIE DES POLYMÈRES ORGANIQUES (LCPO) UMR5629 UNIVERSITÉ DE BORDEAUX/CNRS/IPB ENSCBP 16 AVENUE PEY BERLAND, PESSAC CEDEX
STEPHANE GRELIER / UNIVERSITY OF BORDEAUX, LABORATOIRE DE CHIMIE DES POLYMÈRES ORGANIQUES (LCPO) UMR5629 UNIVERSITÉ DE BORDEAUX/CNRS/IPB ENSCBP 16 AVENUE PEY BERLAND, PESSAC CEDEX
HENRI CRAMAIL / UNIVERSITY OF BORDEAUX, LABORATOIRE DE CHIMIE DES POLYMÈRES ORGANIQUES (LCPO) UMR5629 UNIVERSITÉ DE BORDEAUX/CNRS/IPB ENSCBP 16 AVENUE PEY BERLAND, PESSAC CEDEX
MICHAEL MEIER / KARLSRUHE INSTITUTE OF TECHNOLOGY, MATERIALWISSENSCHAFTLICHES ZENTRUM MZE, STRASSE AM FORUM, KARLSRUHE

PURPOSE OF THE ABSTRACT

Most of the raw materials used in the chemical industry are petroleum derived. Since petroleum is depleting and related to several environmental problems, an increasing drive towards the use of sustainable alternatives can be recognized. Cellulose is the most abundant organic bio-based material on our planet, with established uses as raw material in the chemical industry. However, the vast potential of this versatile material is limited due to its insolubility and only non-direct processability. Modification of cellulose therefore is one way to achieve desired properties and possible new applications. To have a better control over properties of modified cellulose, homogenous modification is desirable. Various solvents (i.e. N,N-dimethylacetamide-lithium chloride (DMAc-LiCl) or N-methyl morpholine N oxide (NMMO) have been investigated previously.[1] These solvents however suffer from toxicity, instability or difficult recycling and are therefore not considered sustainable solvents for cellulose solubilization. Recently, ionic liquids have been described as ?green? solvents for cellulose solubilization due to their very low vapor pressure and possibility to recycle. Notwithstanding, they suffer from high cost and are easily contaminated in the course of the reaction making their recycling quite challenging. A novel class of so-called CO2 switchable solvents have recently been shown to present a more sustainable route towards cellulose solubilization.[2, 3] We have carried out an optimization study applying such a solvent system via online FT-IR with the aim of a better understanding of the process. Upon optimization, we succeeded to achieve complete cellulose solubilization (up to 8 wt.%) within 10-15 min at 30 °C for the system DBU/CO2.[4] This solvent system offers advantages to traditional ionic liquids: it can solubilize cellulose within 10-15 min at fairly low temperature (30°C) and the precipitation/regeneration of cellulose can be achieved by simply releasing the CO2 pressure. By trapping and isolating the intermediate carbonate formed, we also succeeded to indirectly prove the presence of such intermediates, confirming the reaction mechanism and also offering the possibility of novel modification protocols for synthesis of cellulose carbonates [4]. Furthermore, using this optimized solvent system, we recently reported a sustainable approach for Cellulose aerogel preparation.[5] In another approach, and to ensure sustainability by avoiding derivatization, processable cellulose-materials were prepared via transesterification by using high oleic sunflower oil directly.[6] The subsequent prepared fatty acid cellulose esters (FACEs) films showed very good mechanical stability (elastic modulus up to 480 MPa) and thermal stability (increase by 30 °C

compared to starting cellulose).[6] Finally, in another report, and using multicomponent reactions, we demonstrated the synthesis of multi-functional and processable cellulose-based materials, with tunable Tg [7]. At the end, it is the goal of our investigations on cellulose to ensure sustainability during their chemical transformation, in order to obtain viable and sustainable substitutes for their petroleum alternatives.

FIGURES

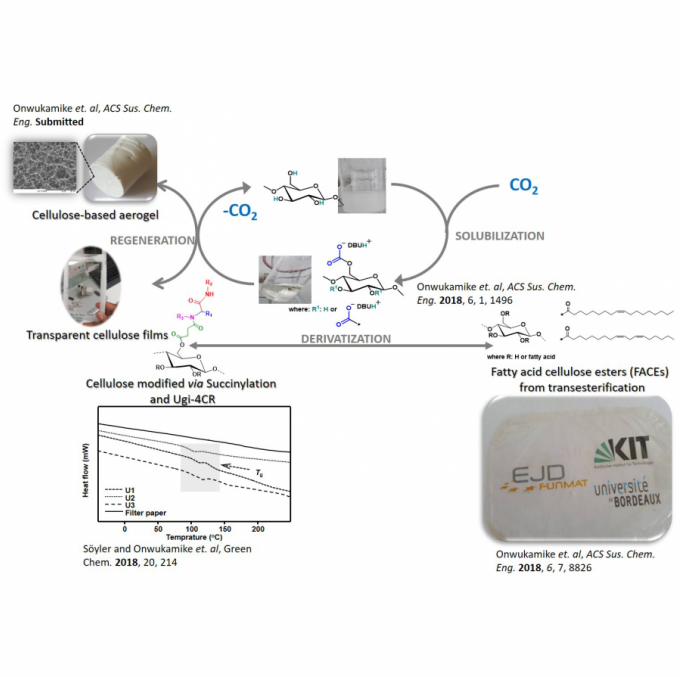

FIGURE 1

General figure for Cellulose Solubilization, Regeneration and Derivatization

General scheme

FIGURE 2

KEYWORDS

Cellulose | Homogeneous modification | CO2 switchable solvent system | Sustainability

BIBLIOGRAPHY

[1] D. Klemm, B. Heublein, H.-P. Fink, A. Bohn., Angew. Chem. Int. Ed, 2005, 44, 3358–3393.

[2] H. Xie, X. Yu, Z. Yang, Z.K. Zhao., Green Chem, 2014, 16, 2422-2427.

[3] Q. Zhang, N.S. Oztekin, J. Barrault, K.D-O. Vigier, F. Jerome., ChemSusChem 2013, 6, 593-596.

4] K.N. Onwukamike, T. Tassaing, S. Grelier, E. Grau, H. Cramail, M.A.R Meier., ACS Sus. Chem. Eng, 2018, 6, 1, 1496-1503.

[5] K.N. Onwukamike, S. Grelier, E. Grau, H. Cramail, M.A.R Meier., ACS Sus. Chem. Eng, (Submitted).

[6] K.N. Onwukamike, S. Grelier, E. Grau, H. Cramail, M.A.R Meier., ACS Sus. Chem. Eng, 2018, 6, 7, 8826-8835.

[7] Z. Söyler, K.N. Onwukamike, S. Grelier, E. Grau, H. Cramail, M. A.R. Meier., Green Chem, 2018, 20, 214-224.