Regeneration of cellulose by water addition to phosphoric acid/cellulose mixture

Gabriella Butera[1], Giulia Cimò[1], Valentina Marsala[1], Claudio De Pasquale[1], Anna Micalizzi[1], Antonella Maccotta[2], Giuseppe Alonzo[1] and Pellegrino Conte[1]

[1] *Dipartimento di Scienze Agrarie e Forestali, Università degli Studi di Palermo, v.le delle Scienze edificio 4, 90128 Palermo*

[2] *Dipartimento di Scienze della Terra e del Mare, Università degli Studi di Palermo, via Archirafi 22, 90123, Palermo, Italy*

In the last years, phosphoric acid has been increasingly considered as a simple and economic solvent for cellulose pretreatment before its degradation to glucose. Cellulose swells in 71–80% phosphoric acid solutions, whereas at higher H_3PO_4 concentrations dissolution appears to occur. In addition, it is reported that regenerated cellulose is more easily fermentable to bioethanol.

The aim of the present study was to elucidate the mechanism for cellulose regeneration following treatment with phosphoric acid at room temperature.

CPMAS ^{13}C NMR spectra revealed a downfield shift of the ^{13}C NMR signals from the regenerated cellulose as compared to the crystalline one. CPMAS ^{31}P NMR spectroscopy showed presence of organic phosphate in the regenerated cellulose. These results suggested that cellulose regeneration consisted in the precipitation of a phosphorylated polymer. Fast field cycling NMR relaxometry confirmed such hypothesis. In fact, the correlation time of water saturated crystalline cellulose was shorter than that measured for the water saturated regenerated cellulose. The phosphate groups bound to the regenerated cellulose surface allow restriction of water mobility, thereby producing longer correlation times.

Finally turbidimetric analyses revealed that the mechanism of regeneration consisted in a first reduction of the colloidal cellulose size followed by aggregation, colloidal size increment and flocculation.

This study is of paramount importance to understand how phosphoric acid interact with cellulose in order to address its possible uses in biomass transformation for bioenergy purposes.

Keywords: micro-cristalline cellulose; NMR; H_3PO_4.