The relevance of structural features of cellulose and its interactions to dissolution, regeneration, gelation and plasticization phenomena

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Cellulose is known to be insoluble in water and in many organic solvents, but can be dissolved in a number of solvents of intermediate properties, like N-methylmorpholine N-oxide (NMMO) and ionic liquids (ILs) which, apparently, are not clearly related. Cellulose can also be dissolved in water at extreme pHs, in particular if a cosolute of intermediate polarity is added. We review the main achievements in the dissolution area and discuss underlying mechanisms. In the past, cellulose insolubility has often been referred to strong hydrogen-bonding between cellulose molecules and dissolution has been discussed in terms of "attack" (by for example OH^- ions) on these hydrogen bonds. We demonstrate that this is not a suitable starting point. On the contrary, recent work has much emphasized the role of cellulose charge and the concomitant ion entropy effects, as well as hydrophobic interactions. Thus we argue that cellulose is significantly amphiphilic as supported by solubility in the presence of acids and bases with organic counterions, for example tetrabutylammonium hydroxide. Ionization of cellulose has been a long debated issue but recent NMR work has given clear support for deprotonation at high pH. In addition to presenting recent work on novel cellulose solvents we illustrate the association and precipitation of cellulose from rheology studies, and how they can be affected by other amphiphilic compounds. Cellulose dissolution and regeneration have had important applications for a long time. By dissolution in aqueous media further uses become possible. In this work we have explored cellulose dissolution under aqueous alkaline conditions with urea as a solution-promoting cosolute of intermediate polarity. We have considered the co-regeneration of cellulose with another polysaccharide to prepare novel renewable materials. Cellulose-chitosan nanocomposite particles and films were successfully prepared for the first time. Via mixing of the biopolymer solutions, emulsification (w/o) and regeneration by temperature induced sol-gel transition followed by addition of an antisolvent, spherical microparticles were obtained. Films were cast and regenerated. Using tuned protocols, different particle sizes, biopolymer distribution, porosity and mechanical performance could be obtained. Direct evidence for the hydrophobic properties of cellulose is indicated in the adsorption at the oil-water interface, as deduced from the interfacial tension. Based on this the ability of molecular cellulose to stabilize emulsions has been examined.

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