Wettability behavior of lignin-cellulose composites obtained after supercritical water hydrolysis of birch wood.

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1. Introduction

The contact angle technique is a well-known and commonly used method for the direct determination of surface wettability and the understanding of the surface properties of polymers. It is a quick, inexpensive and relatively simple technique which has been shown as advantageous in obtaining information about the structure of the matrix, especially when dealing with biopolymer substrates^{1,2}. Further, numerous of studies have already been made referring to the temperature dependence of water contact angle while the effect of pressure remains unclear³.

2. Materials and Methods

This work combines the study of surface properties of lignin and the influence of pressure on the contact angle (CA) between water and the polymer. For this purpose, different lignin polymers were used. Two of the lignin samples (kraft and lignosulfonates) were procured from Sigma and a third sample of lignin was obtained in our lab after Supercritical water hydrolysis of birch wood (SCWL). The SCW treatment of wood primarily hydrolyze the carbohydrates (cellulose and hemicellulose). However, the solids products after SCW treatment are composed of fine particles of both, lignin and cellulose. Depending on the severity of the treatment, the cellulose content can be low (less severe treatment) or high (more severe treatment)⁴. The contact angle measurements were performed using High-Pressure View Cell coupled with high-resolution CCD camera. Measurements were made using sessile drop method at temperature of 25 °C. The pressure dependence of water contact angles is commonly investigated in CO₂ atmosphere. However, N₂ was used in this study in the pressure range from atmospheric pressure to 50 bar. The time dependence of contact angle was also monitored over a period of approximately 10 min.

3. Results and discussion

Considering the generally accepted rule that solid surfaces with $CA < 90^{\circ}$ are considered hydrophilic, while surfaces with $CA > 90^{\circ}$ are considered hydrophobic, the results showed that all tested samples are hydrophilic with average initial contact angle for all tested pressures approximately 43.7° (±2.5°). Figure 1 displays water droplet images recorded immediately after droplet deposition (A and C) and after approximately 10 min of analysis (B and D). Although, there is no significant differences between the initial contact angle of different polymer samples, as time progresses, SCWL shows a higher contact angle compare to kraft lignin. In addition, a different trend in the change of contact angle with time can also be notice. Such results suggest a significant structural difference of SCWL and Kraft lignin. SCWL is a very complex mixtures of different types of chemicals and polymeric lignin⁴. Our results for pressure dependence were compared with data available in literature. So far, it can be noticed that our results differ from literature. At a certain temperature, literature shows that the CA increases very slightly with rising pressure and becomes more significant at higher pressure¹. These differences could be attributed to the different gas employed to pressurize the system. When the pressure is increased with carbon dioxide, this will partially dissolve in water change the pH of it. This effect would likely affect the CA and the interaction of the liquid with the polymer. In addition, the higher pressure the high carbon dioxide dissolved in water and higher potential pH change. In our case, the gas employed to pressurize the system was nitrogen, considered an inert and then not affecting the pH. Also, it should be considered that the tested polymers surfaces are more complex. Additional measurements at higher pressure will be taken.



4. Conclusions

In this moment it is difficult to make clear conclusions. However, it is obvious that lignin obtained after SCW hydrolysis showed different behavior during CA measurements which is clearly related to different chemical structure compare to commercial lignins. From the other side, pressure independence can be explained by the gas involved in pressurize the system and complex surface structure. Namely, under tested conditions, nitrogen is poorly soluble in water and without effect on the PH. As a consequence, pressure change showed no effect on CA.

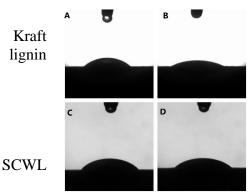


Figure 1. water droplet images captured immediately after droplet deposition (A and C) and after approximately 10min of analysis (B and D).

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