FORMATION OF HYDROXYPROPYLATED STARCH FILMS; STRUCTURE EVOLUTION DURING THE CASTING

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Casting is an attractive method to prepare thin films from drying a concentrated solution. However crystallization or retrogradation of starch in the form of a B-crystalline structure can occur during the drying step thus influencing the properties of the film[1]. The objectives of this study were to understand mechanisms occurring during film formation while drying took place.
In the present work, films of hydroxypropylated and hydrolysed pea starch with mean molecular weights $\overline{M}_w$ of 5×10^4 g/ mol and 1.5×10^5 g/mol were prepared by drying the solutions (concentration: 25%) at 25°C and 40% of Relative Humidity. The drying kinetics was monitored through the mass variations while the crystallinity evolution was followed by Wide angle X-Ray Diffraction (WXRD). The properties of the films were characterised by sorption isotherms and Differential Scanning Calorimetry (DSC).
Cast-films exhibited a B-type crystalline structure. Cristallinity was of 18% for the highest molar weight sample and 24% for the lowest. Sorption isotherms were similar for both samples. The variations of the Glass transition temperature Tg with the water content from 6% to 23% (wet basis) showed a strong plasticizing effect of water. In this water content range, the Tg also decreased of about 5°C with decreasing $\overline{M}_w$. From these Tg variations of HPPS as a function of the water content and the variations of the water content as a function of drying time, we could follow the Tg variations of HPPS during the drying process and build a drying state diagram. Tg increased with drying time as a result of the decrease of the water content in the system. From the state diagram, we can determine a critical water content of about 20% for which Tg of HPPS is equal to 25°C, the drying temperature. This was reached at a drying time of around 8h and was slightly lowered with decreasing $\overline{M}_w$. WXRD performed during the drying process evidenced that the structure of the system evoluted during the casting from an initially amorphous state to a semi-cristalline state. It was found that the crystallinity evolution during the casting process was stopped at around 9h, this time being also reached sooner for the lowest molecular weight sample. These results are in agreement with the transition time obtained from the drying state diagram. This study can provide tools to choose drying parameters in order to optimize the structure and properties of HPPS cast films.

References

1. Å. Rindlav, S. H. D. Hulleman and P. Gatenholm, *Carbohydrate Polymers*, **1997**, *34, (1-2), 25-30*