Chapter 3

Recrystallisation of starch studied with MDSC

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Introduction

In starch-based biodegradable polymers, the crystallisation of starch has an influence on the texture of the product \cite{1, 2}. For use as a material a controlled crystallisation can be a benefit since it can improve the mechanical properties. In food the retrogradation is undesirable as it is one of the reasons of firming. Investigation of the parameters that have an influence on the crystallisation behaviour of starch are thus of great interest, since they enable to understand and to control the structure development of the material.

The native semi-crystalline morphology of starch granules is destroyed in the so-called gelatinisation process, by applying heat in the presence of water or other additives \cite{3}. The amorphous starch system can be (re)crystallised in a consecutive thermal process. The accompanying physical events are termed retrogradation \cite{4}.

Different analytical techniques have been used to study the crystallisation of starch. X-ray being one of the most common techniques \cite{5}. Colwell et al. were the first to investigate the ageing of wheat starch gels by differential thermal analysis \cite{6}. Other techniques used are differential scanning calorimetry (DSC) \cite{7–10}, nuclear magnetic resonance \cite{11}, rheometry \cite{12}, microscopy \cite{4}, Raman \cite{13}, infra-red spectroscopy \cite{14} and isothermal micro-calorimetry \cite{15}.

Crystallisation studies at high starch concentrations have only been reported occasionally \cite{8, 16–19}. A majority of research has been carried out on diluted systems, containing 30\% of starch or less. For such diluted starch systems, turbidity measurements are often used to determine retrogradation \cite{20}. Crystallisation rates are mostly determined at two different temperature ranges of interest in the daily application: 1°C to 5°C (refrigerator) and 20°C to 25°C (room temperature). It is however impossible to get a global overview of the influence of different parameters on the crystallisation kinetics, by analysing data

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of which the crystallisation rates have been determined only at these temperatures. However some trends have been proposed and various models to describe the (re)crystallisation mechanism of starch have been formulated. Although a lot of information is available on the crystallisation of starch, the influence of parameters like the crystallisation temperature, the glass transition temperature, the concentration, and the type of starch and additives still needs to be better understood. More recently, the importance of the glass transition temperature in understanding the crystallisation process, has led to the study of more concentrated systems [9, 10].

The knowledge of the exact value of the glass transition, $T_g$, is very important in the choice of appropriate ageing conditions, because crystallisation will occur between $T_g$ and the melting temperature, $T_m$. In excess of water, below the maximal freeze concentration, $C_g'$ (73 w%) [7, 18, 21], starch and water phase separate. $T_g$ of the system was suggested to remain constant [1] instead of following the curve towards $T_g$ of water. The minimum $T_g$ is reported to be that of the maximal freeze concentrated phase, called $T_g'$. Under these conditions the crystallisation and melting of phase separated water is overlapping with $T_g$ of plasticized starch. This makes it more difficult to measure $T_g$ for these systems [18].

Remark that is very difficult to measure $T_g$ of carbohydrates very precisely [22], for several reasons. First of all, $T_g$ is very sensitive to moisture content as explained above. Evaporation of water during the analysis should therefore be prevented. To obtain these conditions, changes to the existing equipment are sometimes necessary.

Secondly, most products degrade at rather low temperatures [23–25]. Heating the samples to high temperatures during the analysis should therefore be avoided. $T_g$ of dry starch can only be estimated by extrapolation [18, 21, 26–29] since the thermal degradation of starch at temperatures below $T_g$ precludes investigation of the dry material [24–30].

Another difficulty is the fact that $T_g$ of many products is smeared out over a broad temperature range, due to the high polydispersity of many natural materials [31]. It is also suggested that, as moisture content is lowered, the distribution of water in starch becomes very heterogeneous (distribution of $T_g$'s), which also broadens the $T_g$ range [32].

Several analytical techniques have been used to investigate the glass transition of carbohydrates. Most commonly, Differential Scanning Calorimetry (DSC) has been utilised [18, 26, 30, 33–35]. Since $T_g$ is sometimes difficult to identify with DSC for the reasons mentioned above and due to the fact that the change in $C_p$ at $T_g$ is small [30], a combination with for instance Dynamic Mechanical Analysis [36] (DMA) may be necessary. Many other methods to determine Tg values have been used in literature, like Nuclear Magnetic Resonance [37] (NMR), Thermal Mechanical Analysis [38] (TMA), Dielectric Analysis [39] (DEA), and Mechanical Analysis [27]. All these techniques have advantages and disadvantages.