

The influence of plasticisers on the molecular organisation in starch based products

A.L.M. SMITS¹, S.H.D. HULLEMAN², J.J.G. VAN SOEST²,
J.F.G. VLIEGENTHART¹

¹ *Bijvoet Centre for Biomolecular Research, Utrecht University,
P.O. Box 80075, 3508 TB Utrecht, The Netherlands*

² *Agrotechnological Research Institute ATO-DLO,
P.O. Box 17, 6700 AA Wageningen, The Netherlands*

ABSTRACT

Physical ageing and retrogradation of starch materials was investigated with solid state NMR spectroscopic techniques. CP/MAS and HP/DEC spectra provided information on the crystallinity and the extent of structuring in the material. With relaxation time measurements mobility changes and variations in domain sizes during ageing were observed, elucidating the ageing processes. Together with changes in the polysaccharide mobility, the plasticiser mobility and their interaction can be examined with solid state NMR spectroscopy.

INTRODUCTION

Plants produce starch by photosynthesis in order to store energy. It occurs as granules that are primarily composed of two polysaccharides, amylose and amylopectin. Starch can be used to replace common polymers. In the food industry it is used as a natural food-thickener, and it is a main energy provider in the human diet.

Ageing, causing the staling of bakery products and the embrittlement of starch plastics, deteriorates the properties of these products. To gain fundamental insight into the molecular processes underlying physical ageing and retrogradation of starch based products, the influence of polyols as plasticisers on the molecular organisation in the products is investigated with modern, complementary analytical techniques. Especially advanced solid state nuclear magnetic resonance spectroscopy (NMR) offers new opportunities. Compression moulded starch-

glycerol materials with low water contents were considered as model systems for starch plastics (Van Soest *et al.*, 1997), while starch-maltose gelatinised materials were taken as a model for bakery systems. The materials were aged at various humidities, keeping them at specified conditions with respect to their glass transitions (T_g).

During sub- T_g physical ageing molecular rearrangements take place, that can be observed e.g. by a sub- T_g endotherm in DSC (Thiewes *et al.*, 1997). Retrogradation results in the recrystallisation of amylose and amylopectin, yielding characteristic melting peaks in DSC. From X-ray diffraction the extents of recrystallisation after retrogradation can be determined. Peak positions and peak intensities from IR spectra are different for different crystallinities, making IR a technique for examining ageing phenomena on a short-range molecular level. With solid state NMR spectroscopy (changes in) the molecular mobility is observed and the amounts of crystalline and amorphous material can be determined. Chemical shifts, lineshapes and linewidths provide information on intermolecular chain packing, the ratio of crystalline to amorphous material and on sample anisotropy. Relaxation times are short for mobile and longer for more rigid material, yielding information on the molecular mobility.

Solid state NMR spectroscopic techniques have lead to new insights into both ageing processes, keeping in mind that physical ageing takes place below the products glass transition, in the glassy state, whereas retrogradation takes place above its T_g . A method for investigating changes in not only the polysaccharide but also the plasticiser mobility is discussed. The molecular processes underlying physical ageing and retrogradation of gelatinised starch systems are partly elucidated and can be related to the ageing of starch based bakery products.

MATERIALS AND METHODS

Model starch systems are prepared by mixing potato starch with water, giving a 10% dry weight starch dispersion. Maltose or glycerol is used in some samples as a plasticiser in weight ratio 30 plasticiser: 100 dry starch. The systems are gelatinised in a Brabender viscometer. The mixture is stirred with 75 rpm and heated to 90°C with 2°C/min, and held at 90°C for 55 minutes, when the viscosity has reached a constant value. The products are freeze dried to a water content of 11% and aged at 30% and 90% relative humidity (RH), keeping the systems below and above their glass-transitions (T_g), respectively.

Solid state NMR spectra were collected on a Bruker AMX 400 operating at 400 and 100.63 MHz for ^1H and ^{13}C . Samples were spun at the magic angle (54.7°) with respect to the static magnetic field. Carbon and proton 90° pulse lengths were 5 μs . Carbon chemical shifts were determined relative to tetramethylsilane, TMS, using solid glycine at room temperature as

external reference. Samples were packed into 7mm ceramic rotors and spun at 3-4 kHz. In ^{13}C CP/MAS experiments cross polarisation time was set to 2 ms and the recycle delay to 2s.

RESULTS

Solid state NMR spectroscopy is a good technique for observing molecular changes during ageing, by means of spectral changes in lineshapes and linewidths and by changes in relaxation times. CP/MAS allows the observation of the less mobile parts of a sample, whereas the more mobile sites are detected with HP/DEC. Changes in peak intensities during ageing involve mobility changes due to ordering of the material. Also, different crystal structures can be identified, because of different peak splitting due to a difference in the number of glucose units in the crystal cell.

When using glycerol as a plasticiser, it is possible to follow the plasticiser mobility, since glycerol has other chemical shifts than starch (fig. 1). Mobility changes in the starch polysaccharides and glycerol can be simultaneously determined. This allows the investigation of the influence of plasticisers on starch ageing.

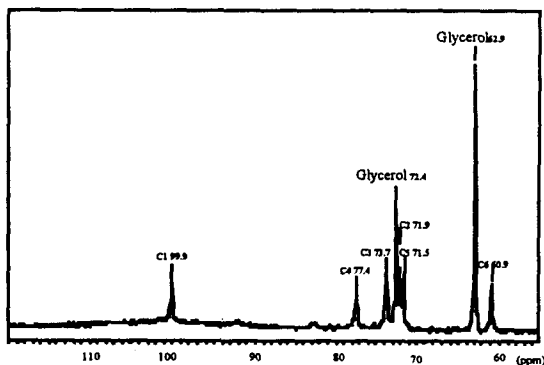


Figure 1. HP/DEC spectrum of potato starch with glycerol

Relaxation times provide information on mobility changes and changes in domain sizes. Increased relaxation times suggest a lower mobility or larger domains. Freeze dried gelatinised starch was aged at 30% and 90% RH (fig. 2). When the material was aged at 30% RH the samples were below their T_g and the observed increase in $T_{1\rho}$ during the first two weeks was due to a decrease in free volume or the development of plasticiser-polymer interactions. When conditioned at 90% RH an initial increase in $T_{1\rho}$ is suggested, which is due to increasing domain

sizes when water is absorbed in the glassy state. When enough water is absorbed, the glass-rubber transition takes place and the further absorption of water increased the molecular mobility, decreasing $T_{1\rho}$. Due to retrogradation the molecular mobility decreased and an increase in $T_{1\rho}$ was observed.

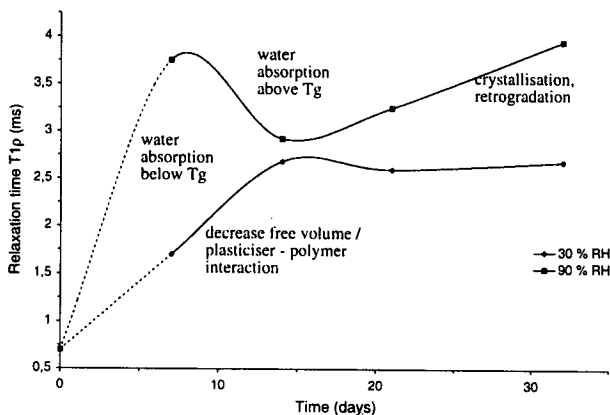


Figure 2. Relaxation times of conditioned gelatinised potato starch

CONCLUSIONS

Physical ageing and retrogradation were examined with solid state NMR spectroscopic techniques. Relaxation times provided important information on both ageing processes. The types of interactions of plasticisers with the starch polysaccharides and their localisation can be cleared up. With the knowledge of molecular processing underlying ageing and the role of plasticisers, ageing can be reduced or prevented, increasing the utility of starch.

ACKNOWLEDGEMENT

We thank ATO-DLO for the use of their facilities and technology foundation STW for financial support.

REFERENCES

- THIEWES H.J., STEENEKEN P.A.M., 1997. The glass transition and sub- T_g endotherm of amorphous and native potato starch at low moisture content. *Carboh. Pol.* 32, 123-130.
- VAN SOEST J.J.G., BORGER D.B., 1997. Structure and properties of compression-moulded thermoplastic starch materials from normal and high-amylose maize starches. *J. Appl. Pol. Sci.* 64 (4), 631-644.