

The Influence of Polyols on the Molecular Organization in Starch-based Plastics

Angela L. M. Smits^{1*}, Stephan H. D. Hulleman², Jeroen J. G. Van Soest², Herman Feil² and Johannes F. G. Vliegenthart¹

¹Bijvoet Centre for Biomolecular Research, University Utrecht, PO. Box 80.075, 3508 TB Utrecht, The Netherlands

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

ABSTRACT

The effect of processing temperature and time on the B-type crystallinity of thermoplastic starch was studied by recording X-ray diffractograms of conditioned, compression molded starch systems containing glycerol and water as plasticizers at a ratio of 100:30:56 (w/w/w). Initial recrystallization, developed during molding, was investigated further on similar amorphous potato starch and potato amylopectin systems. The crystallinity prior to processing does not influence the recrystallization, though residual (granular) crystallinity, present due to incomplete melting, increases the total crystallinity. After molding at high temperatures (>160°C), amylose is mainly responsible for initial recrystallization in the B-type lattice. The observed degree of recrystallization, however, cannot be due to amylose crystallization alone. Amylose seems to serve as a nucleus for crystallization of amylopectin or amylose-amylopectin co-crystallization takes place.

Thermally induced starch polysaccharide-glycerol interactions were investigated on mixtures of dried starch and glycerol using differential scanning calorimetry and solid-state nuclear magnetic resonance spectroscopy. An exothermal transition was observed after which the mobility of glycerol was decreased significantly. This indicated the development of a strong

polysaccharide-glycerol interaction in the absence of water. Copyright © 1999 John Wiley & Sons, Ltd.

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INTRODUCTION

Starch can be molded into biodegradable products, using standard equipment used for the processing of synthetic polymers. The produced starch plastics are complex systems because of the wide range of structures that can occur due to variations in processing conditions, such as temperature and water content, and due to differences in composition of the starch source used, such as the water and lipid contents, and morphology [1–3]. The limited knowledge of the relations between processing conditions and the structure and properties of starch-based plastics makes it difficult to predict and control the mechanical properties. Furthermore, aging causes embrittlement of starch plastics, deteriorating the properties of the products [4, 5].

It is known that parameters such as the starch source (amount of amylopectin and amylose, presence of fatty acids), the processing temperature, the water content during and after processing, and time strongly determine the crystallinity and therewith the mechanical properties of the produced viscoelastic semicrystalline starch plastics. During processing, single-helical amylose crystal-

* Correspondence to: A. L. M. Smits, Bijvoet Centre for Biomolecular Research, University of Utrecht, PO Box 80.075, 3508 TB Utrecht, The Netherlands.
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linity (V_a , V_h , and E_h type) can be induced, depending on the amylose content, the level of thermomechanical input, and the presence of low-molecular weight complexing agents (fatty acids, monoglycerides) [6]. Residual and time-induced double helical (B-type) crystallinity can be present, depending on the starch source and the plasticizer content [7].

It is proposed that the crystallinity of thermoplastic starch strongly determines the mechanical properties. Therefore, insight into the effect of starch composition, processing parameters and time on the B-type crystallinity and into the plasticizer-macromolecule interaction is essential for optimizing and broadening the use of thermoplastic starch by controlling the molecular structure in the material. The interaction of glycerol with starch polysaccharides (amylose and amylopectin) and structural changes in thermoplastic starch during storage were investigated as a part of a larger project concerning the influence of polyols on the molecular organization in starch-based products with applications to food and nonfood products.

EXPERIMENTAL

Thermoplastic starch samples were prepared by compression molding native potato starch (Avebe, NL) with glycerol (Boom, NL) and deionized water at a dry matter:glycerol:water ratio of 100:30:56 (w/w/w), or native potato starch (Avebe), amorphous potato starch (Flocgel LV-W, Avebe) or potato amylopectin (Avebe) with glycerol and deionized water at a ratio of 100:30:30 (w/w/w), at different temperatures. The ingredients were mixed and left to settle 24 h before processing. A PHI press, type 75U1209S-2JCS-J-Y2-S5-7, with a mold of $150 \times 100 \times 1 \text{ mm}^3$ (exterior dimensions $350 \times 300 \text{ mm}^2$) containing 30 g premix was used. At 4 t pressure (on the total mold surface) the temperature was increased to 100°C at 10°C/min. Then, the pressure was increased to 40 t and the temperature increased further to the set cure temperature. After curing for 15 min, the samples were cooled to room temperature at 10–15°C/min for 8 min. The samples were stored at 20°C and 90% relative humidity (RH). At these controlled conditions, the water content remained 30 wt%. Structural changes in time were investigated using X-ray powder diffraction.

Dry starch-glycerol samples were prepared by physically mixing glycerol with native potato starch that was dried 48 h at 40°C in a vacuum-oven at a dry matter:glycerol ratio of 100:30 (w/w). The samples were examined using differential scanning calorimetry (DSC) and solid-state nuclear magnetic resonance (NMR) spectroscopy.

X-ray powder diffractograms were recorded on a Philips PC-APD diffractometer in the reflection geometry in the angular range 4–40° (2θ). The CuK_α radiation from the anode operating at 40 kV and 50 mA was monochromized using a 15 μm Ni foil.

The diffractometer parameters were: divergence slit 1°, receiving slit 0.2 mm and scatter slit 1°. A proportional detector was used to detect the scattered radiation. Diffractograms were baseline corrected by drawing a straight line between the intensities at 7 and 40° (2θ). The ratio of the height of the crystalline diffraction at 17.3° (2θ) and the height of the total diffraction at this angle is defined as the crystallinity index, a measure for the amount of B-type crystallinity of the sample.

Differential scanning calorimetry was performed on a Perkin-Elmer DSC 7 robotic system. Samples were prepared in stainless steel 60 μl DSC cups. They were heated at 10°C/min from 20°C to 180°C, kept at that temperature for 5 min, cooled at 50°C/min to 20°C and heated to 180°C at 10°C/min.

Solid-state ^{13}C -NMR spectra were collected on a Bruker AMX 400 operating at 100.63 MHz. Samples were spun at the magic angle (54.7°C) with respect to the static magnetic field. Pulse lengths were 5 μsec in all experiments. Carbon chemical shifts relative to tetramethylsilane (TMS) were determined from the spectra, using solid glycine at room temperature as external reference. Samples were packed into 7 mm ceramic rotors and spun at 3–4 kHz. In ^{13}C cross-polarization, magic angle spinning (CP/MAS) experiments the cross-polarization time was set to 2 msec and the recycle delay to 2 sec.

RESULTS AND DISCUSSION

Structural changes in thermoplastic starch during storage were investigated on compression molded potato starch samples containing glycerol and water at a dry matter:glycerol:water ratio of 100:30:56 (w/w/w). With polarized light microscopy residual granular crystallinity was observed depending on the molding temperature [3]. From X-ray diffraction it was concluded that during processing considerable initial (B-type) recrystallization takes place followed by time-induced recrystallization (retrogradation) during the first days of storage (Fig. 1). The initial recrystallization was determined directly after cooling the samples in the mold.

Since it was not expected to find a higher initial recrystallization for samples cured at higher temperatures, this feature was investigated more thoroughly by compression molding similar regular potato starch, amorphous potato starch and potato amylopectin mixtures with glycerol and water at a ratio of 100:30:30 (w/w/w) at various temperatures (Fig. 2) [8]. It was found that initial recrystallization takes place irrespective of the crystallinity before molding, since it was also found for the amorphous potato starch samples. At higher molding temperatures, more initial recrystallization was observed for regular and amorphous potato starch, but for potato amylopectin a decrease in recrystallization was found for increasing molding temperatures. Amylose seemed to be necessary for initial recrystallization into the B-type lattice

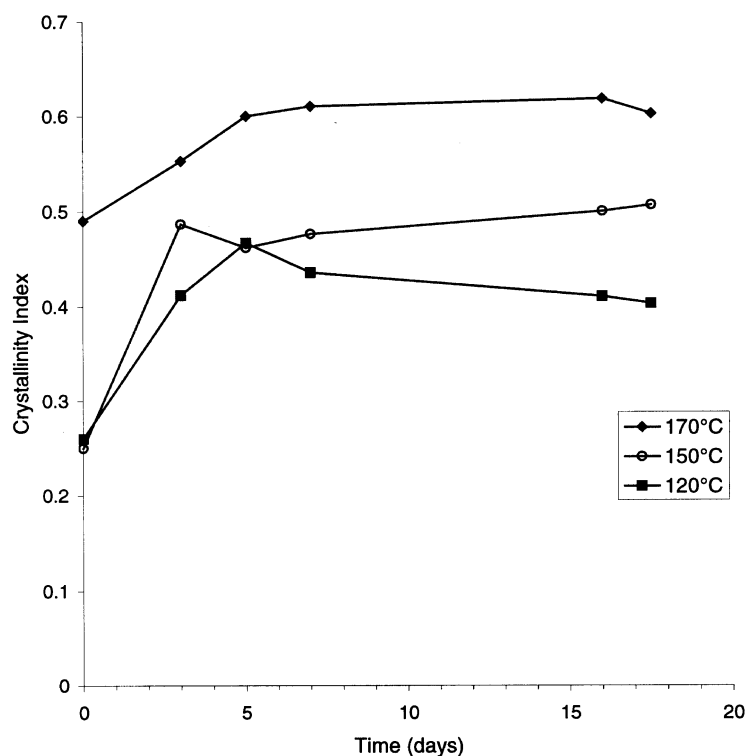


FIGURE 1. Recrystallization in time as determined with X-ray powder diffraction of compression molded potato starch with glycerol and water at a ratio of 100:30:56 (w/w/w), conditioned at 20°C and 90% RH. Examined molding temperatures were 120, 150 and 170°C.

after molding at high temperatures. The observed recrystallization of regular and amorphous potato starch was higher than could be attributed to amylose alone. Therefore it is suggested that amylose serves as a nucleus for amylopectin crystallization or amylose-amylopectin co-crystallization takes place.

Samples cured at temperatures above the

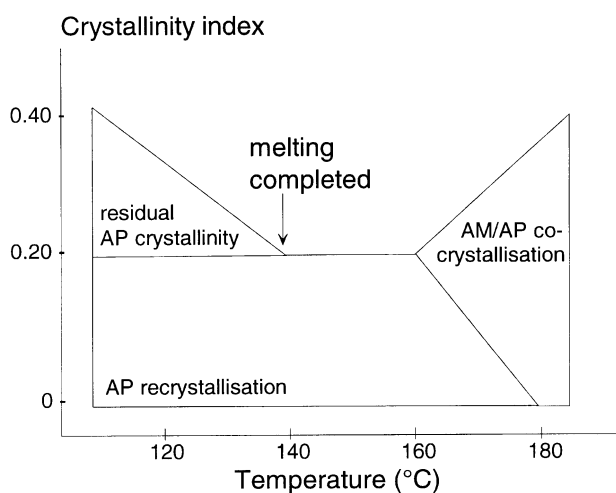


FIGURE 2. Schematic description of the contribution of the different starch components (AM = amylose, AP = amylopectin) to the crystallinity as determined with X-ray powder diffraction directly after compression molding potato starch with glycerol and water at a ratio of 100:30:30 (w/w/w) at various temperatures.

melting-range of starch recrystallized more when their cure temperature was higher. Since they are all amorphous, and all go through the same melting-range at equal speed upon cooling, equal recrystallization was expected. We suggest that a decrease in molecular weight, owing to degradation, causes an increase in recrystallization, because shorter molecular chains crystallize more easily than long chains.

The interaction of glycerol with starch polysaccharides (amylose and amylopectin) was examined using DSC and solid-state NMR spectroscopy. DSC on physically mixed dry starch with glycerol showed a strong exothermal transition, as depicted in Fig. 3 for dried potato starch with glycerol at a ratio of 100:30 (w/w). The transition was irrever-

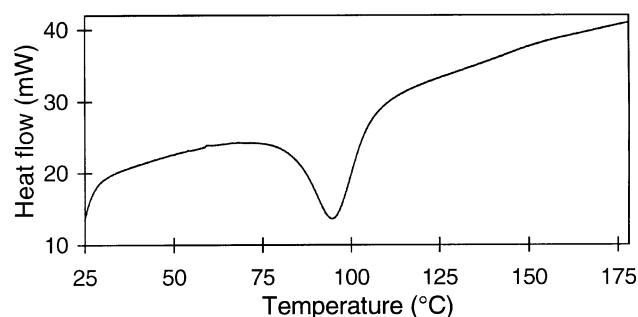


FIGURE 3. Exothermal transition observed with DSC at a heating rate of 10°C/min of physically mixed dried potato starch (0 wt% H₂O) with glycerol at a ratio of 100:30 (w/w).

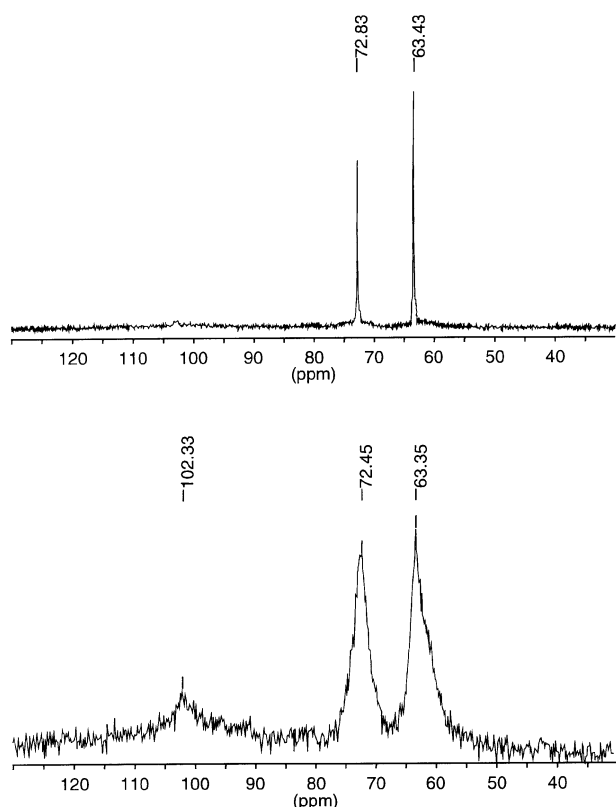


FIGURE 4. HP/DEC solid-state ^{13}C -NMR spectra of dried potato starch (0 wt% H_2O) with glycerol at a ratio of 100:30 (w/w) before (top) and after (bottom) heating above the exothermal transition.

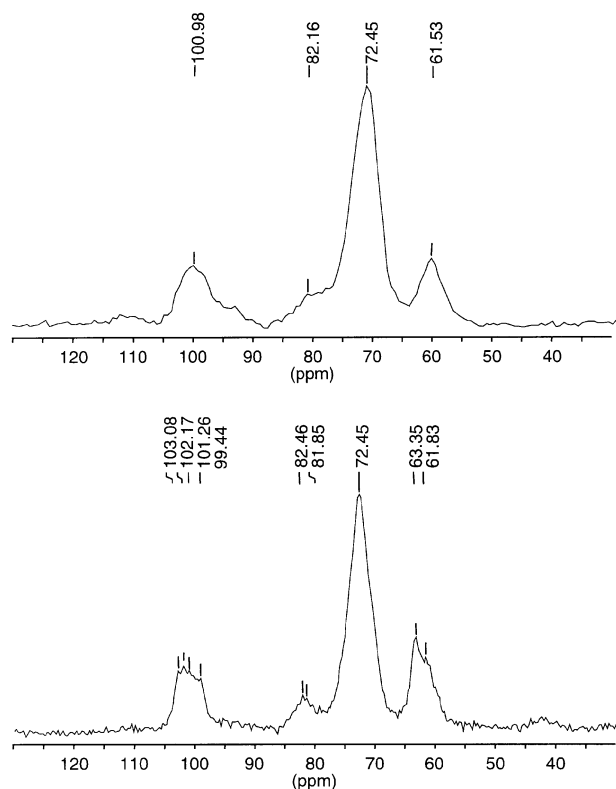


FIGURE 5. CP/MAS solid-state ^{13}C -NMR spectra of dried potato starch (0 wt% H_2O) with glycerol at a ratio of 100:30 (w/w) before (top) and after (bottom) heating above the exothermal transition.

sible, as it was not observed during rescanning of the sample.

The transition enthalpy was proportional to the amount of glycerol added, suggesting that glycerol is responsible for the observed exotherm. With solid-state NMR spectroscopy, changes in the material were investigated by analyzing the mixtures before and after heating above the exothermal transition. The more crystalline material was observed using CP/MAS pulse sequences and the more flexible parts were observed using high power decoupling (HP/DEC) pulse sequences [9–11]. With HP/DEC, sharp glycerol peaks were observed prior to the transition, which became less intense and broader after the transition. This indicates a decrease in the glycerol flexibility (Fig. 4). In the CP/MAS spectrum, glycerol peaks appeared after the exothermal transition, e.g. at $\delta = 63.35$ ppm, indicating a conformational limitation (immobilization) of glycerol (Fig. 5). The observed mobility changes of the polyol plasticizer indicate a strong polysaccharide–glycerol interaction. After the addition of water, the changes in glycerol mobility due to the exothermal transition are reversed, and then in the absence of water strong starch–glycerol interaction is disrupted.

In this research, insight into starch recrystallization and molecular ordering due to starch–plasticizer interactions is obtained. It is shown that the control of starch recrystallization and ordering is possible by means of variation of the processing temperature and the use of plasticizers. Continuing research on the molecular structure in starch-based systems will improve the control of the product mechanical properties, and therewith the use of various starches for different applications can be expanded.

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