STRUCTURAL PROPERTIES OF PLASTICIZED STARCH: XRD AND SOLID-STATE NMR STUDY

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1. Introduction

Starch has attracted a lot of attention as an available polymer from renewable resources that might be used as a potential material for plastic production. Although pure starch films can be prepared [1], native starch has poor processibility and mechanical properties of its end products [2,3] due to strong interactions between starch chains which cause brittleness of starch materials. Plasticizers, such as water, polyols or amide-groups containing molecules [4-10] are commonly used to reduce the intermolecular forces in starch and increase film flexibility. The processing of native starch known as gelatinization requires also thermomechanical treatment during which the phase transition of starch occurs.

Native starch is a semi-crystalline polymer. The crystallinity mostly comes from highly-branched amylopectin, which is a polymer consisting of D-glucose units linked by α(1-4) and α(1-6) bonds [11,12]. Pending chains of amylopectin form double-helices which are crystallized either in a monoclinic (A-type) or in a hexagonal lattice (B-type crystalline polymorph), depending on starch source. The main structural differences between the polymorphs are higher packing density of double-helices and fewer water molecules between the helices in A compared to B polymorph. C polymorph is also observed; it is a mixture of A and B type structures. There are strong intermolecular hydrogen links between hydroxyl groups in these structures which hinder the movements of starch chains. The other polymer present in starch is mostly linear amylose consisting of D-glucose units linked by α(1-4) bonds. In presence of small molecules like lipids, amylose forms a single helix with the complexing agent inside a helix channel [11]. Amylose and branching parts of amylopectin form amorphous zones in native starch granules.

During the gelatinization, added plasticizer forms hydrogen bonds with starch hydroxyl groups while increasing intermolecular spacing in double-helices which results into increased mobility of starch chains. As a result, highly-ordered starch structure is completely or partially destroyed at multiple levels [13] and native starch is converted into a thermoplastic material. On the other hand, fast amylose single-helical crystallization into several types of V-type polymorphs was observed during starch plasticization [6]. Depending on processing and storage conditions, thermoplastic starch (TPS) might recrystallize with rearranging of plasticizer molecules after a period of time [7,14]. This process known as retrogradation causes embrittlement of TPS and is common when glycerol as a plasticizer is used [14,15]. Urea is thought to prevent starch retrogradation [15,16] but it is solid with little internal flexibility and thus should not add much flexibility to TPS.

In this paper, corn starch plasticized with glycerol, urea or their mixture is studied. The effect of plasticizer content on structural properties of TPS using nuclear magnetic resonance (NMR) methods and X-ray diffraction (XRD) is discussed.

2. Experimental

Native corn starch Meritena containing ~25 % of amylose was used in this study. TPS were prepared by compression molding method. Mixture of starch, selected plasticizer and

water was gelatinized at 60 °C and then mixed at 130 °C at 100 rpm for 10 minutes. The processed sample was hot pressed at 130 °C and 100 kPa into plates and dried at 90 °C for 4 hours. The ratio of plasticizers and native starch varied according to Table 1. The contents of materials are referred to weight contents and the mass of plasticizers is based on the mass of starch.

The solid-state ^{13}C NMR measurements were performed on a 400 MHz Varian NMR solid-state spectrometer operating at the resonance frequency of about 100 MHz and at the magic angle spinning (MAS) frequency of 10 kHz. 4 mm ZrO_2 rotors were used and ^{1}H-^{13}C cross-polarization (CP) was applied. The CP contact time was 1 ms with a relaxation delay of 8 s and proton decoupling of 83 kHz. Acquisition time was 20 ms. Chemical shifts in the spectra were referred to TMS.

After a period of storage time, samples were scanned by Rigaku MiniFlex 600 X-ray powder diffractometer operating at Cu Kα wavelength of 0.154 nm with Ni filter for CuKβ filtering. Diffraction patterns were recorded in the angular range 2θ = 5 – 40° with a speed of 5°/min and step interval of 0.01°. The X-ray generator operating conditions were 40 kV and 15 mA.

Tab. 1. *Composition of the TPS and % content of ordered-phase calculated from the NMR spectra.*

Sample identification	Starch (wt%)	Plasticizer content (wt%)		% Content of ordered-phase (NMR)
		Glycerol	Urea	
NS	100	-	-	56
GTPS	100	60	-	58
UGTPS	100	30	30	37
UTPS4	100	-	40	29
UTPS6	100	-	60	25
UTPS8	100	-	80	23

3. Results and discussion

Fig. 1 shows X-ray diffractograms of the native corn starch (NS) and plasticized samples. NS exhibits a clear A-type polymorph signature in the diffractogram with reflections particularly at $2\theta \sim 15.1°$, 17.1°, 18.1° and 22.9° as expected for corn starch [12,17]. B-type polymorph is usually recognized by typical reflections at $2\theta \sim 14.6°$ and 16.9° with additional peaks at $2\theta \sim 10.0°$, 11.0°, 13.9°, 22.3°, 23.7° and 26.2° [17]. GTPS and UTPS6 show strong reflections at 14.1° and 16.9° and thus subscribe to the B-type polymorph. It is commonly believed that plasticized starches after the preparation are mostly amorphous due to disruption of ordered starch structure during the gelatinization and that crystalline structure transforms with storage time [6,7]. Depending on plasticization and storage conditions, different crystallinity and crystalline structure can be evolved in the plasticized samples compared to native starch [1,9,16,18,19]. Native corn starch plasticized by glycerol lost the A-type crystallinity during the processing and recrystallized into the B-type structure as shown in Fig. 1 for GTPS. Unlike the glycerol, urea was previously observed to prevent starch retrogradation at the RH 50% [9]. However, UTPS6 shows high B-type crystallinity very similar to GTPS (Fig. 1) with additional peaks at $2\theta \sim 22.1°$, 24.5°, 29.5° which were ascribed to separated crystalline urea. High B-crystallinity in UTPS6 was probably evolved during the storage time of 5 months at the relative humidity of ~70%. Higher air humidity could increase the mobility of starch chains and thereby increase starch recrystallization. A similar effect was observed during amylopectin film formation at various RHs [1].

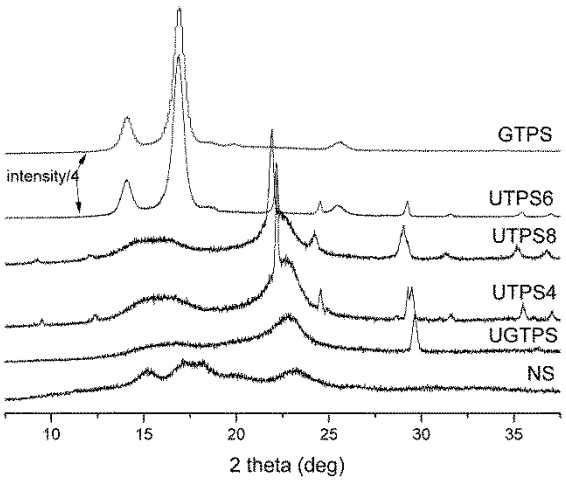

Fig. 1: *The XRD diffractograms of the samples as denoted.*

The other samples (UTPS4, UTPS8 and UGTPS) show presence of separated crystalline urea with reflections in diffractograms at similar positions as UTPS6. The broad bands in the diffractograms at 16° and 23° indicate imperfect A-type crystalline structure in the samples. As mentioned above, crystalline structure of starch is greatly degraded during plasticization. However, a substantial amount of native structure might be still present in plasticized starch [13] as in this case. The broadening of the diffraction peaks could be caused by decreased sizes of crystals and by irregularities within crystals as a consequence of incomplete plasticization process.

While diffraction methods provide insight into long range crystalline order, shorter range subcrystalline order can be probed by NMR spectroscopy. The NMR starch spectra are then a linear combination of signals originating from amorphous and ordered starch phases [17]. The ordered starch phase is represented by single and double helices present also in irregular crystals. Fig. 2 shows CP/MAS ^{13}C NMR spectra of all samples. The major signals in the spectra denoted as $C_1 - C_6$ are related to six carbons in the starch monomer unit as depicted in inset in Fig. 2 [20]. The C_u signal at 162.7 ppm is related to urea carbons [21] and the narrow peaks at 73.2 (C_{g1}) and 63.8 ppm (C_{g2}) correspond to two nonequivalent carbons in glycerol [22]. The intensity ratio of the C_1 signal to the whole starch spectrum after subtracting glycerol and urea signals was ~0.17 for each sample and thus the C_1 signal provides reliable quantitative information on starch structure.

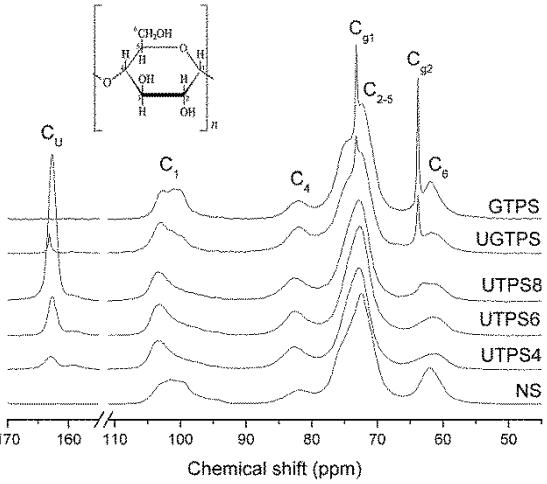

Fig. 2: *CP/MAS ^{13}C NMR spectra of the samples as denoted.*

In Fig. 2, significant changes in the C_1 signal shape for different samples are evident, known to reflect changes in starch structure. The ordered phase is characterized by a triplet and by a doublet appearing in the C_1 spectral region of A and B-type starches, respectively [20]. A triplet appears at ~99, 100 and 101 ppm with intensity ratio 1:1:1 while a doublet appears at ~100 and 101 ppm with intensity ratio 1:1. Spectrum of NS in Fig. 2 exhibits a clear triplet confirming A-type polymorph in agreement with results from XRD. In Fig. 3a, profile of the deconvoluted C_1 signal of NS into ordered and amorphous phase is shown. After a triplet was assigned, three other peaks corresponding to amorphous phase were located at ~94, 97 and 103 ppm. The ordered-phase content was then calculated as the relative intensity contribution of the triplet in the C_1 signal. Similarly, the ordered-phase content was estimated for UTPS4, UTPS8 and UGTPS (Tab. 1). GTPS and UTPS6 showed B-type crystalline structure in the diffractograms. For that reason, a doublet instead of a triplet was assigned in the C_1 region (Fig. 3b).

According to data in Tab. 1, GTPS possess comparable content of ordered-phase as native starch which is in agreement with knowledge that glycerol plasticized starches are prone to fast retrogradation. On the other hand, urea forms more stable bonds with starch than glycerol [9] and thus can prevent starch retrogradation and decrease the ordered-phase content (Tab. 1).

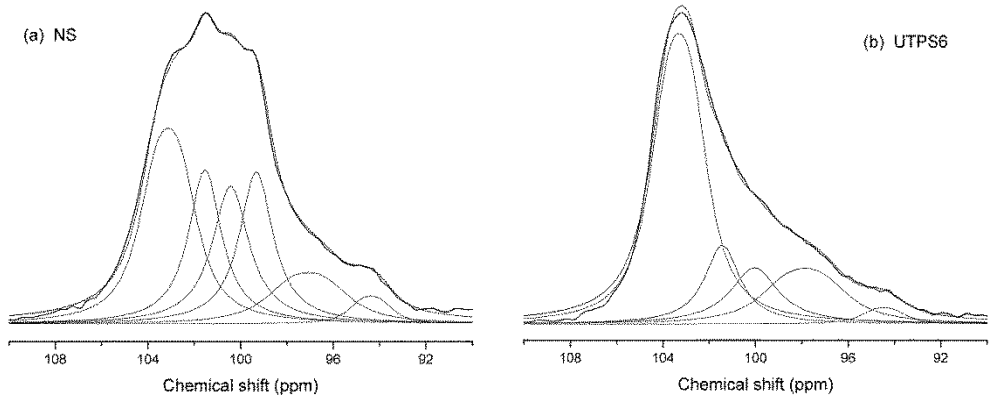

Fig. 3: *The deconvoluted profiles of the C_1 region of (a) NS and (b) UTPS6.*

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