Starch/Alkane Diol Materials: Unexpected Ultraporous Surfaces, Near-Isoporous Cores, and Films Moving on Water

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ABSTRACT: The aim of this study was to find alternative starch plasticizers to glycerol that yielded a less tacky material in high-moisture conditions without leading to starch crystallization. A range of glycerol films containing different potential plasticizers (linear alkane diols) were therefore produced, and it was shown that 1,3-propanediol, in combination with glycerol, was a possible solution to the problem. Several additional interesting features of the starch films were however also revealed. The larger diols, instead of showing plasticizing features, yielded a variety of unexpected structures and film properties. Films with 1,6-hexanediol and 1,7-heptanediol showed an ultraporous film surface and near-isoporous core. The most striking feature was that starch films with these two diols moved/rotated over the surface when placed on water, with no other stimulus than the interaction with water. Films with 1,8-octanediol and 1,10-decanediol did not show these features, but there was clear evidence of a structure with phase-separated crystallized diol in a starch matrix, as observed in high-resolution scanning electron microscopy (SEM) images.

1. INTRODUCTION

The environmental problems associated with plastic waste, microplastics, and incineration of petroleum-based plastics necessitate a change where-by fossil-based plastics are replaced by bio-based (biodegradable) plastics. Starch is an attractive biopolymer due to its abundance in nature and biodegradability, but it is brittle with a high glass-transition temperature and needs a plasticizer for typical plastic applications.1

The plasticization efficiency of glycerol has made it a common additive in thermoplastic starch.2 Its efficiency in polar biopolymers has been documented in many papers, e.g., out of 30 tested potential plasticizers in wheat gluten, glycerol stood out as the most effective candidate, with the largest strain at break.3 In a recent article, we showed with molecular dynamics simulations on a starch (amylopectin) system with six potential plasticizers that its plasticizing effectiveness originated from a comparatively low overall degree of hydrogen bonding, especially with the polymer matrix, short hydrogen-bond lifetime, and molecular flexibility.4 The high plasticization efficiency of glycerol, however, often leads to starch crystallization after gelatinization or with aging/storage time, thereby affecting, e.g., the transparency of cast films and coatings and the mechanical properties.5,6 Under moist conditions, due to its high water miscibility and the resulting low viscosity,7 glycerol also migrates to the film surface, leading to a tacky material and altered film properties.8 At high relative humidities, it can phase-separate with water.9 Alkane diols (e.g., 1,2-ethanediol and 1,3-propanediol) are alternatives which are less effective as a plasticizer compared to glycerol but with less negative side effects (crystallization/tackiness).10−12 In fact, 1,3-propanediol is known to lower the tackiness of glycerol in hygiene/lotion products.13 A drawback with the smaller alkane diols (1,2-ethanediol and 1,3-propanediol) is, however, their relatively low boiling point. They tend to evaporate during high-temperature starch gelatinization. They also are slightly less hydrophilic, with a higher n-octanol/water partition coefficient and total polar area.14

The aim of this study was to investigate if it is possible to minimize the negative side effects of both glycerol and the smaller diols using blends of glycerol and diols (and by adding a low-boiling-point diol to the mixture at a lower temperature after gelatinization) or to use larger diols with higher boiling points. Besides investigating the properties of starch films with 1,2-ethanediol (ETH), 1,3-propanediol (PRO), and their...
mixtures with glycerol (GLY), the properties of the starch materials with larger alkane diols, 1,6-hexanediol (HEX), 1,7-heptanediol (HEP), 1,8-octanediol (OCT), and 1,10-decanediol (DEC), were also investigated. It should be noted that 1,7-heptanediol is a liquid at ambient conditions (if not supercooled, the melting point is $\sim 205^\circ C$) like the smaller diols mentioned above, but the other larger diols are available as crystalline powders. It is noteworthy to mention that 1,8-octanediol has antimicrobial properties and is used to develop antimicrobial composite scaffolds.\textsuperscript{15,16}

It was observed in this work that a mixture of the smaller diols with glycerol yielded plasticized films with less tackiness compared to pure glycerol. Besides this, a number of unexpected results were obtained when investigating the larger diols, including the formation of films with ultraporous surfaces and near-isoporous cores, and films that rotated and moved when placed on a water surface (without any external stimulus).

2. RESULTS AND DISCUSSION

2.1. Diol Evaporation Behavior. The sample prepared with 40 wt % ethanediol had essentially the same thermogravimetric (TG) profile (Figure 1a) as pure starch (Figure S1), indicating that most, or if not all of, the diol evaporated during the film preparation. The sample prepared with 40 wt % propanediol showed a slightly different TG curve, indicating that a small amount of this diol was present in the final film. This is expected since PRO has a higher boiling point (212 $^\circ C$\textsuperscript{17}) than ETH (198 $^\circ C$\textsuperscript{18}). Nevertheless, both films were too brittle to be tensile-tested.

2.2. Mechanical Properties of the Plasticized Starch Samples. The samples containing a mixture of the diol with glycerol were plasticized, and their mechanical properties are given in Figure 2. The fact that the modulus and strength were lower in the films prepared with the propanediol/glycerol mixture than in the corresponding films with the ethanediol/glycerol mixture indicates that propanediol was present to a larger extent than ethanediol in the films with glycerol. The glass-transition temperature (from differential scanning calorimetry (DSC) on films conditioned at 50% relative humidity (RH) and 23 $^\circ C$) was also lower in propanediol systems—GLY10PRO30: $-46^\circ C$, GLY20PRO20: $-60^\circ C$, GLY10ETH30: $-21^\circ C$, GLY20ETH20: $-48^\circ C$. The $T_g$ of GLY20PRO20 was close to that of (dry) starch with 40 wt % glycerol.\textsuperscript{19}

2.3. Surface and Cross-Sectional Morphology. When investigating the starch systems with the larger diols (HEX-DEC), the observations were quite unexpected. A number of different features arose, which caused the focus to be directed more toward these systems. The first thing noted was that the upper surface of the cast films with HEX and HEP was ultraporous (Figure 3c,d). The pores were significantly larger in the HEP40 sample ($19 \pm 10 \mu m$) than in the HEX40 sample ($5 \pm 1 \mu m$). The surface of the pore walls of HEP40 had a birefringent structure, but the main part of the sample was not birefringent (Figures S2b and S2d). This indicates that the pore walls consisted of an oriented/stretched starch or starch/diol structure. Figure S3 shows that the surface pores here were also due to the material fracturing during water evaporation. The reason for the

![Figure 1. TG curves of the different samples: (a) smaller diols and blends with glycerol, (b) larger diols.](https://example.com/figure1)

![Figure 2. Mechanical properties of the plasticized starch samples: (a) stiffness and strength for the different blends, (b) stiffness versus strength.](https://example.com/figure2)
development of crystals in the upper surface is that the density of crystalline OCT (\(\sim 900 \, \text{kg/m}^3\)) is lower than that of water and starch (amylopectin, \(\sim 1450 \, \text{kg/m}^3\)). The HEX40 upper surface “glittered” when illuminated, indicating that, apart from the ultraporous surface, there were regions where HEX had crystallized on top of this structure, which is understandable considering that its density is \(\sim 970 \, \text{kg/m}^3\). The lower side of HEP40 showed droplets of phase-separated diol (Figure S2a). The liquid could also be felt by hand. Clearly, part of the phase-separated portion of the diols was located at one or both sides of the films. The upper surface of the sample with DEC was smoother, with less features than the HEX-OCT samples (Figure 3a). The TG curves with a three/two-stage decrease in mass in Figure 1b showed that the diols existed as both a phase-separated structure (first mass loss) and in a molecularly mixed phase with starch (second mass loss).

The film cross sections of OCT40 (Figures 4b and S4) and DEC40 (Figures 4a and S5) showed a clear phase-separated structure in the core with diol particles “trapped” inside the starch-rich matrix. The DEC crystals are somewhat heavier (density, \(\sim 1100 \, \text{kg/m}^3\)) than OCT crystals, which is probably why the former are more evenly dispersed through the thickness of the sample, without large crystals segregated at the upper surface. The comparatively lower content of diol at the upper surface in the DEC40 sample is probably why the upper surface was smoother with less pores generated during water evaporation. In both OCT40 and DEC40, the particle size distribution was very large, from a few to more than 100 \(\mu\text{m}\) in the largest dimension/direction (Figures 4a,b, S4, and S5). The side view in the DEC40 images also revealed a porous surface layer on the lower side, containing 500–700 nm wide sheets (Figure S5 and inset in Figure 4a).

The cross section of the HEX40 and HEP40 films revealed a large number of pores with a relatively uniform size (near-isoporous structure), with sizes (measured in random directions) of 2.0 ± 0.6 \(\mu\text{m}\) for HEX40 and 6 ± 2 \(\mu\text{m}\) for HEP40 (Figure 4c,d). It is apparent that most pores were empty. The reason for the development of the pores in the core of the HEX40 and HEP40 samples is not fully clear. They were formed in the last drying step at 50 °C since the solution was transparent before being inserted in the oven. Also, they must have been formed early in this last step since most pores were elongated in the horizontal direction and clearly affected by gravity exerted by the starch/diol mixture before it solidified. As mentioned above and indicated by TG (Figure 1b) and DSC (below), there was partial phase separation between HEX/HEP and the starch, but only very few pores contained any diol. There are at least two possible reasons for the pore formation: (1) phase separation of water (droplets) that later evaporated (it is known that there are capillary channels in the system from solvent uptake measurements (see below), which may have been generated by the evaporating water) and (2) phase separation of diol, which was redissolved in the starch-rich matrix during later stages of film formation/drying. It should be noted that, at 50 °C drying, both diols are liquid. The presence of the larger diols (HEX-DEC) implies a starch–diol system that is less polar than pure starch or the starch system with the smaller diols (here ETH and PRO). Thus, water is more likely to phase-separate in the former system during the drying/evaporation process. The droplet-like porous surface in the HEX40 and HEP40 samples is most certainly the effect of the evaporation of phase-separated water droplets (Figure 3). The use of smaller more polar ETH and PRO favored molecular mixing in the starch–diol–water system, and hence no pores were formed in these films (exemplified in Figure 4e). The larger surface pores in the HEP40 film compared to those in the HEX40 film, together
with pores in the core, could then be explained by the larger degree of phase separation of water during the drying process in the more nonpolar HEP40 system.

By analyzing the top and side views of the films using SEM images, it was possible to estimate a surface “pore volume” per surface area, which was significantly higher for HEP40 (155 μm³/μm²) than for HEX40 (ca. 42 μm³/μm²).

2.4. X-ray Diffraction and IR Analyses. The phase-separated OCT and DEC crystallized during the 50 °C drying period (the mixtures were transparent before entering the oven). Note also that a sizable fraction of the trapped crystallized OCT and DEC particles or empty pores were also elongated in the horizontal direction (Figures 4a,b, S4, and S5). The melting points of OCT and DEC were 72 °C and 60−62 °C, respectively, in both the pure state (as-received powder, DSC curves not shown here) and in the starch samples (Figure S6). HEX40 has a melting point of 42 °C, which means that it, as mentioned above, crystallized after the solidification of the film (Figure S6). The HEP remained liquid in the final film, as observed by all characterizations, except after the supercooling took place in the DSC measurements. The melting point was essentially at room temperature (22 °C, Figure S6). It was noted that the uneven carbon number (here seven carbons, HEP) yielded the least stable crystals (lowest melting point). As expected, no crystalline peaks were observed in the X-ray diffraction curve of the HEP40 film (Figure 5a), in contrast to those of the HEX40, OCT40, and DEC40 materials (Figure 5b). It should also be pointed out that, among the plasticized films, the GLY10PRO30 film was amorphous, whereas the others contained some crystalline starch material (Figure 5a), which was one of the considerations when considering PRO as a plasticizer.

X-ray diffraction patterns indicated that the diol crystal structures formed in the starch films were different from the crystal structures of the as-received powder (compare Figures 5b and S7). It was, however, difficult to distinguish individual crystal features in the films (a few faceted crystals in the OCT40 sample are shown in Figure S8). The diol crystals observed in the core of the films were often porous, indicating that water was trapped, at least for some time, inside the crystals during the film formation (Figure 6d). Figure 6c shows a quite remarkable birefringent color pattern from the OCT crystals at the upper surface.

The IR spectra of the larger diol systems are presented in Figure S8. The broad absorption bands observed around 3300 cm⁻¹ are attributed to the O−H stretching, and are affected by the hydrogen-bond structure. Two sharp peaks (3380 and 3321 cm⁻¹) appeared, which originate from O−H stretches in the crystalline phase. They were present in the pure powders and in the starch−diol mixtures with a crystalline diol phase (HEX40, OCT40, and DEC40). The spectra were similar on both sides of the HEX40 and HEP40 samples, showing that both starch and diol were present at the surfaces (the sampling depth of the attenuated total reflection-infrared (ATR-IR) depends on, e.g., the wavelength, but is typically ca. 1−5 μm). Features of both components were also present in the upper surface of both OCT40 (also the lower surface) and DEC40 film, but the lower surface of DEC40 (not shown) had essentially a pure starch spectrum, verifying that the lower porous layer (Figures 4a and S5) was mainly, if not fully, pure starch.

2.5. Unexpected Behavior of the Films Exposed to Water and n-Heptane. It was of interest to find out how the phase-separated structures in the larger diol systems affected...
the behavior of the material in contact with water. Pure starch films, when placed on a water surface, curled, and then occasionally straightened out again (Figure 7a–d). The films containing HEX and HEP curled/bent less (Figures 7e and S10), and the bending direction was independent of which surface was facing the water surface. Simple swelling of the part facing the water surface would lead to a curl and bend in the opposite direction, which indicates that surface tension possibly also played a role in the behavior of both the pure starch and starch–diol films. Apart from the bending, the HEX40 and HEP40 films, when placed on the water surface, started to rotate/spin and move over the water surface, as illustrated in Video 1, without any external stimulus other than the presence of water. The time-dependent uptake resulted in small shape changes in the film, which triggered motion of the film over the surface. The motion ceased after some time, probably because the sample became saturated with water. This motion over the water surface was not observed for the DEC40 film, and it remained straight (the OCT40 sample could not be evaluated here because of a very fragmented film). It is notable that the HEP40 film went from opaque white to transparent after a few minutes in water (Figure S11), which suggests that the pores inside were filled with water, reducing any light scattering from the otherwise empty pores. The film remained transparent when dried, which indicates that the pores collapsed due to capillary effects when the water evaporated. Visual inspection of the water showed that diol was also migrating from the sample to the water phase. It was not possible to determine the densities of the films using the Archimedes principle, since they rapidly absorbed both water and nonpolar liquids. In fact, the “capillary-driven uptake”, measured by immersing the sample for 1 s in water and n-heptane, was significant (Figure 8). The proof of capillary action is the fact that the rapid uptake was higher for n-heptane than for water, despite the polarity of the films. Hence, in the larger diol systems (HEX–DEC), many pores were available for the liquid through “capillaries” as well as, in the case of water, through “normal” diffusion through the bulk material. The rapid uptake was highest in the DEC40 sample (could not be measured in the fragmented OCT-40 film), which indicates that the capillaries were, in this case at least, partly the “interphase” between starch and the phase-separated diol particles. These are especially clearly observed in the surface of OCT40 and DEC40 (Figure 3a,b) and in the particle containing pores in the core (Figure 6d).

**Figure 7.** Shape of a pure starch film put on a water surface (a–d) and the shape of HEX40 and HEP40 (e) and DEC40 (f).

**Figure 8.** Instantaneous (1 s) water and n-heptane uptake versus the size of the diol molecule (trans conformation). Filled and unfilled symbols refer to n-heptane and water uptake, respectively. The uptake includes both surface liquid and liquid absorbed in the film.

3. CONCLUSIONS

1. It is shown in this work that the structure developed in situ during the preparation of the starch–diol films yielded unique features. This was especially the case for the 1,6-hexanediol and 1,7-heptanediol systems. Both systems yielded an ultraporous surface, and the fractured cross-sectional surfaces had a near-isoporosity structure.

2. The two diols in (1) yielded films that moved over the surface of water without any external force (only triggered by water–material interactions). By learning more about this behavior, it may be possible to develop actuators driven by only the presence of water. In addition, possible applications of the materials, considering solely the surface and core porosity of the films and the ease of forming these, could be as rapid absorbents of, e.g., hydrophobic substances (e.g., oil), template for different chemical reactions, controlled-release applications, water sensor (goes from opaque to transparent in water), and in lightweight structures.

3. The water-triggered motions were not observed for the DEC40 film (this effect could not be evaluated for OCT40, because of the highly fragmented film). None of the HEX–DEC diols yielded any plasticizer effects.

4. Starch plasticization occurring with the two smallest diols, in combination with glycerol, was a consequence of the absence of phase separation and, consequently, a high degree of molecular mixing.

4. EXPERIMENTAL SECTION

4.1. Materials and Film Preparation. Starch (amylopectin (AP) from waxy maize [CAS: 9037-22-3]) and 1,10-decanediol, 98% [CAS: 112-47-0]; 1,8-octanediol, 98% [CAS:
629-41-4; 1,7-heptanediol, 95% [CAS: 629-30-1]; 1,6-hexanediol, ≥99% [CAS: 629-11-8]; 1,3-propanediol, 98% [CAS: 504-63-2]; and 1,2-ethanediol (ethylene glycol), ≥99% [CAS: 107-21-1] were purchased from Sigma-Aldrich. Glycerol, ≥99% [CAS: 56-21-5] was purchased from Alfa Aesar. The starch–diluent materials were labeled DECCXX (DEC: 1,10-decanediol), OCTXX (OCT: 1,8-octanediol), HEPXX (HEP: 1,7-heptanediol), HEXXX (HEX: 1,6-hexanediol), PROXX (PRO: 1,3-propanediol), ETHXX (ETH: ethanediol), and GLYXX (GLY: glycerol), where “XX” is the wt % diol. Starch with the glycerol–diol mixtures were labeled GLYXXETHXX and GLYXXPROXX.

The films were prepared by casting an aqueous solution of 1 wt % amylopectin (with respect to total weight of solution) and diol/glycerol (total weight of 40 wt % with respect to total dry mass of amylopectin and diol/glycerol) into Petri dishes. Plasticizer (40 wt %) was used to avoid the transition region where plasticization sets in, which occurs between 20 and 30 wt % glycerol. First, the solution was heated to 90 ± 3 °C at a rate of 5 °C/min and maintained at that temperature for at least 15 min until a clear mixture was observed, indicating a gelatinized system. The systems with a diol and glycerol (GLY10PRO30, GLY20PRO20, GLY10ETH30, and GLY20ETH20) were prepared by the same method, but the diol (PRO or ETH) was added under stirring after cooling the solution to 70 °C and again maintained for at least 15 min at that temperature. The gelatinized solution was allowed to cool to ca. 60 °C and subsequently poured into Petri dishes (which were coated with polytetrafluoroethylene supported by an aluminum foil (Bytac Z-27, Saint-Gobain Performance Plastics Corp.)) and then placed in an oven at 50 °C to dry them fast enough to avoid/minimize starch crystallization.

4.2. X-ray Diffraction (XRD). An ARL X’tra X-ray diffractometer was used to carry out X-ray diffraction of the samples. The instrument was operated at 40 kV and 45 mA, with Cu Kα radiation, which has a radiation wavelength of 1.54 Å. A continuous slit aperture technique with a θ−2θ Bragg–Brentano-based geometry was used to remove Cu Kα radiation. High resolution was provided by a Peltier cooled Si(Li) solid-state detector without using diffracted beam monochromators or β-filters. The measured angle range was 5°–40° with a step width of 0.045° and a measuring rate of 2.7 °C/min.

4.3. Differential Scanning Calorimetry (DSC). Differential scanning calorimetry was conducted with a Mettler Toledo DSC1. The starch films were conditioned at 23 °C and 50% relative humidity (RH) and tested in sealed aluminum hermetically sealed TGA pans (DEC: 1,10-decanediol), OCTXX (OCT: 1,8-octanediol), HEPXX (HEP: 1,7-heptanediol), HEXXX (HEX: 1,6-hexanediol), PROXX (PRO: 1,3-propanediol), ETHXX (ETH: ethanediol), and GLYXX (GLY: glycerol), where “XX” is the wt % diol.

4.4. Thermogravimetric Analysis (TGA). Thermogravimetric analysis was performed with a Mettler Toledo TGA. Samples with a weight of 8 ± 0.5 mg were placed on 70 μm ceramic cups. All runs were performed with the same method, meaning a ramp in temperature from 30 to 600 °C at a rate of 10 °C/min under an inert atmosphere (nitrogen, with a purge rate of 50 mL/min).

4.5. Fourier Transform Infrared (FTIR) Spectroscopy. FTIR spectroscopy was conducted with a PerkinElmer Spectrum 100 instrument, equipped with a triglycerine sulfate (TGS) detector and a Golden Gate unit (single-reflection ATR). The spectrum was obtained from 16 consecutive scans between 4000 and 600 cm⁻¹ with a scanning step of 1.0 cm⁻¹ and a resolution of 4.0 cm⁻¹. The samples were conditioned at 23 °C and 50% RH for at least 48 h before the FTIR measurements.

4.6. Tensile Testing. An Instron S944 tensile test instrument was used to measure stress–strain properties at 23 °C and 50% RH with a 500 N load cell. Straight specimens were cut from the films (length, 30–35 mm; width, 4 mm) and tested using a gauge length of 25 mm and a strain rate of 25 mm/min according to ASTM D882. A Mitutoyo 10C-1128 micrometer was used to measure the thickness of the films, and five replicates of each material were tested.

4.7. Scanning Electron Microscopy (SEM) and Light Microscopy. The film surface and cross-section were investigated using a Hitachi S-4800 field emission scanning electron microscope (FE-SEM) operating at 10 kV, with a 6 mm working distance in backscattering mode. Pieces of the films were placed on conductive carbon tape for analysis of the surface morphology. For studying the specimens’ cross sections, the films were immersed in liquid nitrogen for 5 min, cryo-fractured, and then placed on conductive carbon tape. A voltage of 3 kV and a current of 10 μA were used. The materials were sputtered with a palladium/platinum (Pt/Pd) target in an Agar high-resolution sputter coater before insertion in the SEM. The coating time was 45 s, leading to a conductive surface layer of ca. 2 nm. The size of the different features observed in the FE-SEM was estimated using ImageJ software. The size of pores and particles were obtained from 50 measurements on each material. Light microscopy images were obtained with a Leica DM IL LED Fluo inverted microscope.
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Notes
The authors declare no competing financial interest.

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