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Compression Molding and Tensile Properties of Thermoplastic Potato Starch Materials

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The mechanical and melt flow properties of two thermoplastic potato starch materials with different amylose contents were evaluated. The materials were prepared by mixing starch, glycerol, and water, mainly in the weight proportions of 10:3:4.5. Compression molding was used to produce sheets/films with a thickness in the range of 0.3−1 mm. After conditioning at 53% relative humidity (RH) and 23 °C, the glycerol-plasticized sheets with a higher amylose content (HAP) were stronger and stiffer than the normal thermoplastic starch (NPS) with an amylose content typical for common potato starch. The tensile modulus at 53% RH was about 160 MPa for the high-amylose material and about 120 MPa for the plasticized NPS. The strain at break was about 50% for both materials. The stress at break was substantially higher for the HAP materials than for the NPS materials, 9.8 and 4.7 MPa, respectively. Capillary viscometry at 140 °C showed that the high-amylose material had a higher melt viscosity and was more shear-thinning than the NPS. Dynamic mechanical measurements indicated a broad transition temperature range for both types of starch material. The main transition peaks for glycerol-plasticized starch were located at about room temperature with the transition for the HAP material being at a somewhat higher temperature than that of the NPS material with a lower amylose content. It was also noted that the processing conditions used during the compression molding markedly affected the mechanical properties of the starch material.

Introduction

Starch is a biodegradable material produced in many different crop plants. Since it is biodegradable, inexpensive, has good oxygen-barrier properties, and comes from a renewable source, it would generally be reasonable to use starch materials in, for instance, packaging applications. A major drawback of starch is its high hygroscopicity and its sensitivity as a mechanical and barrier material to water or moisture.[1,2]

Native starch films containing low amounts of water are often brittle and, to reduce the brittleness, plasticizers such as glycerol have been used. Another way to modify the material is to alter its molecular constitution with regard to chain length, number of branch points, branch lengths, etc.[3] Native starch extracted from plants is organized in semicrystalline granules with a typical size in the 1−100 μm range.[4] This original structure can be disrupted by heating and shearing giving a thermoplastic melt. This can be accomplished with a conventional extruder (or similar equipment) used for processing thermoplastics.[5,6]

Starch contains two major types of polymers, amylose and amylopectin. The relative proportions of these polymers depend on the origin (the crop plant) of the starch. Both polymers are built-up by anhydroglucose units linked together by α-D glycoside bonds. Amylose is a linear polymer with α-1,4 linkages between the anhydroglucose units, and its molecular mass is typically in the range of 10^5−10^6 g/mol. Amylopectin is an extensively branched polymer. It has a backbone structure of α-1,4 linkages between the anhydroglucose units with branching at the α-1,6 position. The molecular mass of amylopectin is high, typically in the range of 10^7−10^8 g/mol.[4]

Higher strength and toughness are expected from thermoplastic starch materials with a higher amylose content possibly associated with a more entangled starch network.[3,7] Other reasons for this difference are also possible as will be discussed later. This improvement in mechanical performance would thus in principle extend the potential applications of starch. Most studies of thermoplastic high-amylose starch have been carried out on corn starches.[8−10] In the present work, potato starches with two different amylose contents have been used, and the objective was to assess and compare the mechanical and melt rheological properties of a thermoplastic material based on high-amylose potato starch with those of a normal potato starch.

Experimental Section

Materials. High-amylose potato starch (HAP) and normal potato starch (NPS) were supplied by Lyckeby Stärkelsen, Kristianstad, Sweden. According to the supplier, the HAP had an amylose content of about 86 wt %, whereas the NPS had an amylose content of about 21 wt %.[11] Glycerol type Rectapur supplied from Prolabo, Sweden was used as plasticizer for the starch (together with deionized tap water).

Preparation of Thermoplastic Starch Sheets. Starch, glycerol, and water were premixed by hand in proportions of 10:3:4.5 (by weight), and a nominal moisture content of approximately 26 wt % was achieved. Starch without glycerol was also mixed with water in proportions of 10:0:8 giving a nominal water content of about 45 wt %. The weight proportions are used in the following to denote the samples. Two series of NPS materials with different moisture contents (10:3:2.5 and 10:3:6.5), but with the same glycerol content, were also prepared. The mixtures were blended in a Brabender chamber mixer, Brabender OHG, Duisburg, Germany, at 140 °C, 50 rpm for 3 min. The molten material was compression molded into sheets with a Bucher heated hydraulic press, Bucher-Guyer AG, Niederweningen, Switzerland at, 140 °C and 9 MPa for 5 min. In some cases, process temperatures of 120 or 180 °C were used. The material was cooled under pressure to 30 °C, which took approximately 15 min. The pressure was then released, and the sheet was peeled away from the press plates. The thickness of the sheets was typically 0.3−1 mm.

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Methods. *Water Content.* The water content of the starch samples was gravimetrically determined after they had been stored at 110 °C for 12 h using a Mettler M3 TG50 thermobalance thermogravimetric analyzer (TGA), Mettler Instrumente AG, Grefensee, Switzerland.

Conditioning of the Specimens. Some of the specimens were conditioned in closed chambers over saturated salt solutions at 21 ± 2 °C. The salts used were $MgCl_2$, $Mg(NO_3)_2$, and $SrCl_2$ giving relative humidities (RH) of 30%, 53%, and 70%, respectively.[12] A Firlabo SP-BVEHF climate-controlled chamber, Société Firlabo, Meyzieu, France, was also used for the conditioning.

Capillary Viscometry. The melt viscosity was measured as a function of the shear rate with a Ceast rheoscope 1000 6742/00, Ceast SpA, Pianezza, Italy, capillary viscometer. The measurements were carried out on pellets cut from pressed sheets with a thickness of the order of 2−3 mm conditioned at 23 °C and 50% RH. Three different capillaries with length-to-diameter ratios of 5, 10, and 40 were used. The diameter of each capillary was 1 mm. The measurements were performed at 120, 140, and 160 °C, and corrections according to Bagley and Rabinowitz were applied. The results were fitted to a power law equation, and the corresponding material parameters K (consistency) and n (flow index) were evaluated.

$$\tau = K\dot{\gamma}^n \tag{1}$$

Here τ denotes the shear stress and $\dot{\gamma}$ the shear rate.

Tensile Properties of the Sheets. Tensile measurements were made on the starch sheets at 23 ± 2 °C and 40 ± 5% RH in an Instron 1193, Instron Ltd., High Wycombe, U.K., according to ISO 527-1, using a strain rate of 6.6×10^{-3} s^{-1}. Samples were cut from the sheets with a cutting die of dog-bone shape. Before the measurements, the samples were conditioned for at least 5 days as described above. The tensile elastic modulus was evaluated from data between 0.05% and 0.25% strain.

Dynamic Mechanical Thermal Analysis (DMTA). For the dynamic mechanical measurements, a strain-controlled rheometer, RSA II analyzer, Rheometrics Inc., Piscataway, NJ, was used. The frequency was 1 Hz, the strain amplitude was 0.05% (in the dual cantilever bending mode), and the temperature range scanned was −100 to 160 °C. Some measurements were also made in the tensile mode (0.06% strain amplitude). The specimens used in the bending mode had a thickness of 1 mm, whereas the thickness of the specimens in the tensile mode was about 0.3 mm. The heating rates used were 10 and 5 °C/min. All samples were covered with silicone grease in order to reduce the water loss during the measurement.[13] The sheet specimens were conditioned at 23 °C and 53% RH for 3−5 days before the measurements.

X-ray Diffraction (XRD). Diffractograms were obtained using a Siemens D8 Advance Theta X-ray diffractometer with a Cr Kα radiation source. An increment step of 0.1° and a rate of 1 step per 10 s were used. Native starch powders and compression-molded samples of NPS 10:3:4.5 and of HAP 10:3:4.5 conditioned at 53% RH for 20 days were used in the experiments The compression-molded samples were milled in a Janke & Kunkel microfine mill, Janke & Kunkel GMBH & CO.KG, Staufen, Germany, with liquid nitrogen in order to produce a powder.

Results

Water Content. For both native NPS and HAP, the equilibrium moisture content at 53% RH and 21 °C was approximately 17 wt %. For starch plasticized with glycerol, i.e., denoted 10:3:4.5, the water content expressed with respect to the total weight of the specimen was 18−19 wt % after conditioning, whereas for conditioned starch plasticized without glycerol (10:0:8), the water content was 12−13 wt %. Gravimetrical measurements indicated that the moisture content of sheets with a thickness of 1 mm or less equilibrated after 2−3 days of conditioning as shown in Figure 1. The major change in water content took place already during the first 24 h.

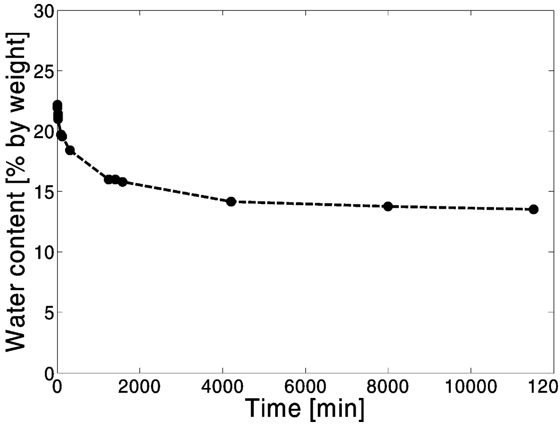

Figure 1. Moisture content as a function of conditioning time at approximately 40% RH for a 0.4 mm thick sheet of NPS 10:3:4.5 after processing.

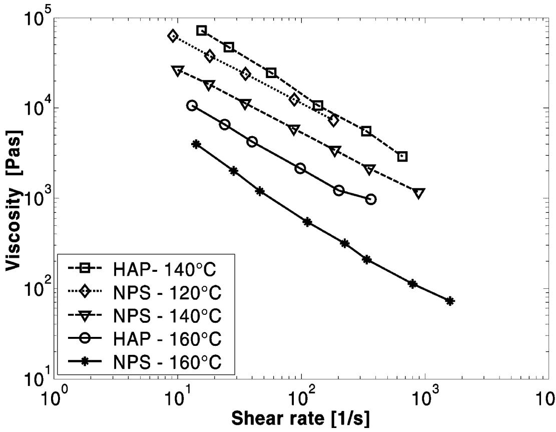

Figure 2. Melt viscosity as a function of the shear rate for HAP and NPS (10:3:4.5). The samples were conditioned prior to the measurements, which means that they contained 18−19% moisture.

Table 1. Power Law Parameters K and n of the Starch Melts (10:3:4.5)

blend	temperature [°C]	K [Pa s^n]	n
NPS	120	172900	0.29
NPS	140	43580	0.32
NPS	160	8512	0.32
HAP	140	130100	0.20
HAP	160	37300	0.29

Capillary Viscometry. The viscosities of the plasticized HAP and NPS samples with the initial composition 10:3:4.5 were determined as a function of the shear rate in the region of 10−1000 s^{-1}. The high-amylose starch samples exhibited a higher viscosity at a given shear rate and temperature, as shown in Figure 2. A more pronounced shear-thinning tendency was noted for HAP than for NPS, especially at 140 °C, as indicated by the lower value of the power law index n, Table 1. Higher temperatures led as expected to lower viscosities at a given shear rate.

Tensile Properties of the Sheets. Glycerol-plasticized HAP (10:3:4.5) samples conditioned at 53% RH and 21 °C exhibited higher values of both elastic modulus and stress at break than the corresponding NPS specimens, see Figure 3. The tensile modulus of NPS 10:3:4.5 was 120 MPa, whereas for HAP 10:3:4.5, it was 160 MPa. The strain at break was 45−50% for both materials.

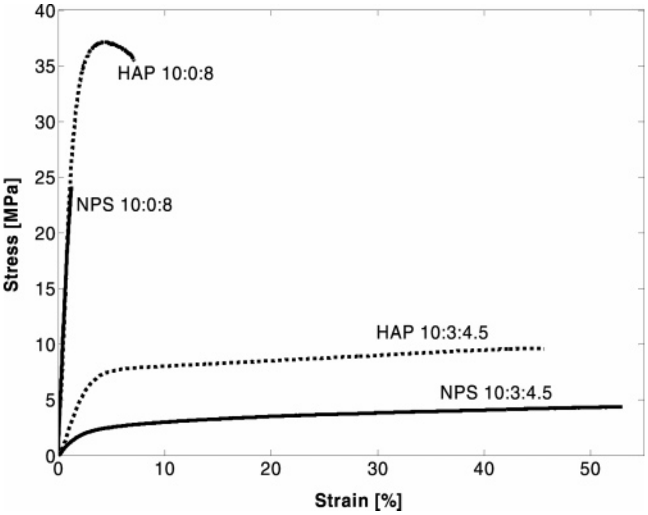

Figure 3. Stress−strain behavior of HAP and NPS (10:3:4.5 and 10:0:8) conditioned at 21 °C and 53% RH.

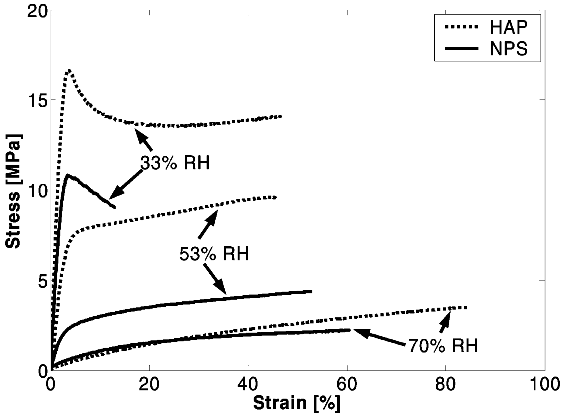

Figure 4. Stress−strain curves for HAP 10:3:4.5 and NPS 10:3:4.5 conditioned at 33%, 53%, and 70% RH.

Omitting the glycerol from the plasticized starches, i.e., using the composition 10:0:8, had quite a drastic effect on the mechanical behavior, as shown in Figure 3. The tensile modulus and strength at break increased markedly for both HAP and NPS, whereas the ultimate elongation decreased. The differences in mechanical properties between the two materials were also less obvious. For example, the tensile elastic moduli of NPS 10:0:8 and HAP 10:0:8 were about 2.3 and 2.5 GPa, respectively. The tensile strength of the starch sheets exceeded 20 MPa in the absence of glycerol.

Since starch is a hygroscopic material, it is expected that conditioning at different relative humidities will affect the resulting moisture content and also the mechanical properties of the compression-molded sheets. The results shown in Figure 4 and summarized in Table 2 illustrate this. A lower moisture content gave significantly higher moduli and strength values, and the elongation at break was reduced. In general, HAP performed better than NPS from a mechanical point of view. The initial composition after blending was in both cases 10:3:4.5. At higher moisture contents, i.e., for specimens conditioned at 70% RH, the differences between HAP and NPS were less than for samples containing less moisture, e.g., those conditioned at 33% RH. In Table 2, it is also obvious that there was in some cases an appreciable scatter in the experimentally determined mechanical parameters. Specimens without glycerol exhibited substantially higher values of ultimate strength and modulus, but also a lower ductility, as described earlier.

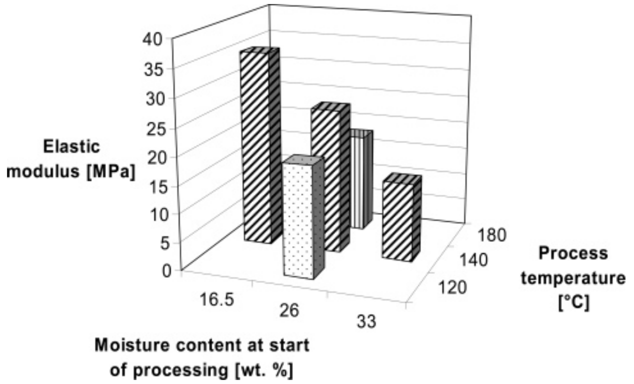

Figure 5. Elastic modulus of thermoplastic NPS sheets containing 30 parts of glycerol per 100 parts (by weight) of starch compression molded at different temperatures and with different initial moisture contents. Standard deviations can be found in Table 3.

Table 3. Tensile Properties of NPS Sheets Containing 30 Parts of Glycerol Per 100 Parts by Weight of Starch Compression Molded at Different Temperatures and with Different Initial Moisture Contents[a]

water content before processing, %	16.5	26	33	26	26
processing temp, °C	140	140	140	120	180
stress at break, MPa	3.0(0.4)	2.1(0.5)	1.7(0.4)	1.8(0.4)	2.0(0.1)
strain at break, %	60(13)	88(47)	164(98)	161(31)	153(12)
elastic modulus, MPa	35(8)	26(5)	14(7)	20(7)	18(3)

[a] The standard deviation is given within the parentheses. The specimens were conditioned at 23 °C and 50% RH before testing.

Influence of Process Conditions on the Tensile Properties. In the case of synthetic polymers, it is known that the process technique and conditions chosen affect the mechanical properties of the material. This also applies to thermoplastic starch, but the situation is somewhat more complex since the initial water content (i.e., before processing the material) also has an effect, as shown in Figure 5 and Table 3. In this series of experiments only NPS was used. The average values of the stress and the strain at break as well as the of elastic modules varied by up to

Table 2. Tensile Properties and Moisture Contents of HAP 10:3:4.5 and NPS 10:3:4.5 Conditioned at Three Different Relative Humidities (Standard Deviations in Parentheses)

material	RH %	moist content, %	maximum stress, MPa	strain at break, %	tensile modulus, MPa	stress at break, MPa
NPS 10:3	33	13.5	11(0.4)	19(4)	564(82)	8.4(0.3)
NPS 10:3	53	18	4.5(0.2)	56(9)	117(29)	4.5(0.2)
NPS 10:3	70	23	2.2(0.3)	53(14)	13(3)	2.2(0.4)
HAP 10:3	33	12	16(0.9)	44(8)	797(53)	14(0.5)
HAP 10:3	53	18	10(0.6)	49(4)	164(30)	10(0.6)
HAP 10:3	70	23	3.0(1.1)	73(35)	11(0.3)	3.0(1.1)
NPS 10:0:8	53	12	25(6.0)	2.2(2.4)	2530(675)	25(2.4)
HAP 10:0:8	53	13	37(5.9)	8.4(7)	2180(669)	33(6.9)

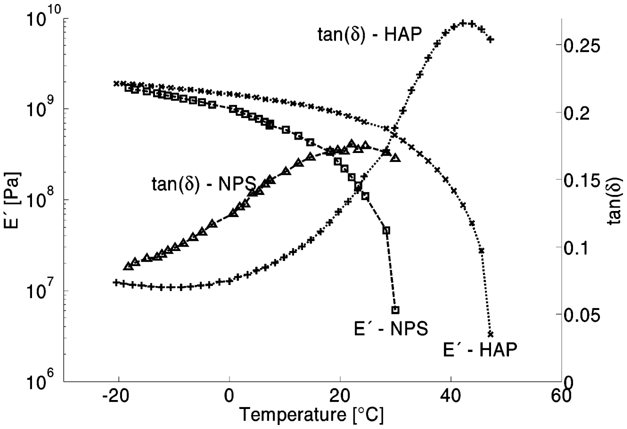

Figure 6. Storage modulus (E') and the loss factor (tan δ) as a function of temperature for conditioned HAP and NPS (both 10:3:4.5). The applied frequency was 1 Hz.

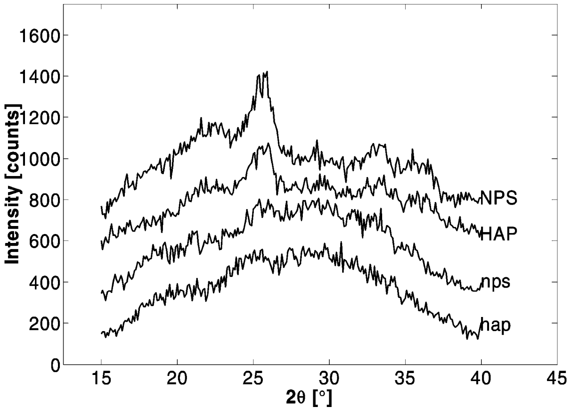

Figure 7. X-ray diffractograms for native NPS starch (NPS), native HAP starch (HAP), and for compression-molded NPS 10:3:4.5 (nps) and HAP 10:3:4.5 (hap) conditioned for 20 days at 53% RH and 23 °C.

about 50% depending on the process conditions, but the variation within each series was also quite large. The stress at break and the elastic modulus increased with decreasing initial moisture content at a given process temperature, whereas the strain at break decreased. A maximum in the stress at break and in the stiffness and a corresponding minimum in the strain at break were noted at the intermediate processing temperature 140 °C, as shown in Figure 5 for the modulus.

The initial moisture content also affected the thickness of the compression-molded sheets after conditioning, although the applied pressure during the compression molding was kept constant. At a constant process temperature of 140 °C, the thickness of the sheets decreased from being more than 1 mm at an initial moisture content of 16.5% to less than or close to 0.5 mm at a moisture content of 33%. This thickness variation may be a result of the higher stiffness of the material at a lower moisture content.

At an initial moisture content of 26%, the thickness of the sheets increased somewhat with increasing process temperature from 120 to 180 °C. This may be associated with a more pronounced steam generation at higher temperatures, leading to a higher melt viscosity.

Dynamic Mechanical Properties of Plasticized Starch. The dynamic mechanical analysis indicated a broad transition ranging over 20−40 °C. The conditioned glycerol-plasticized materials (10:3:4.5) with moisture contents of 18−19 wt % exhibited their main transition temperatures at room temperature or somewhat higher, the NPS material having a lower transition temperature corresponding to a maximum in the loss factor, see Figure 6. A similar shift in the transition temperature has previously been reported by others.[14] At room temperature, the storage modulus was higher for HAP than for NPS, which is in agreement with the results of the tensile tests.

Without glycerol, i.e., for the 10:0:8 materials, the dynamic mechanical measurements indicated that the main transition was above 100 °C. Measurements extending to higher temperatures are however afflicted with some uncertainty, since repeated dynamic mechanical tests on specimens heated to 60−70 °C indicated a shift of the main transition to higher temperature, probably due to a loss of moisture by evaporation. In order for the measurements on these types of material to be more reliable, they should preferably be carried out below 60 °C and, as in this study, a protective coating should be applied to the specimens.[13]

X-ray Diffraction (XRD). In the case of the native NPS and the native HAP, the X-ray diffractograms exhibited a peak at about $2\theta = 26°$, as shown in Figure 7. This corresponds to $2\theta = 17°$ if a Cu Kα radiation source is used. This peak is commonly associated with the B-type crystallinity found in potato starch.[15] The peak intensity was here found to be lower for HAP than for NPS. As most of the crystallinity of the nonprocessed starch is attributed to the amylopectin phase this appears reasonable.[4]

Diffractograms for compression-molded NPS and HAP (both 10:3:4.5) are included in Figure 7. These samples were conditioned at 53% RH and 23 °C for 20 days before measurement. Due to the processing, the intensity of the peaks was reduced indicating a corresponding decrease in crystallinity.

Discussion

The differences in tensile strength and stiffness at room temperature between the glycerol-plasticized HAP and NPS (10:3:4.5) conditioned at 53% RH and 23 °C could be directly related to the differences in the main (or glass) transition temperature (T_g) indicated by the DMTA measurements. The NPS 10:3:4.5 material seems to be within its transition region, whereas HAP 10:3:4.5 is somewhat below its transition at room temperature and therefore has a more glassy character. Higher transition temperatures at higher amylose contents have been observed by others with increases in the range of some 10° which is somewhat lower than found here.[14,16,17] But contradicting results have also been reported; in these cases the differences in transition temperature were greater between amylose and amylopectin.[10,18] DMTA measurements on glycerol-plasticized starch films where the relative humidity was scanned at room temperature showed that the main transition occurred at a lower humidity for amylopectin than for amylose which is in line with the present observations.[13] On the whole, the transitions indicated by DMTA agree with other reported results for glycerol-plasticized starch systems.[19,20]

For specimens conditioned at 70% RH, the difference in tensile behavior between NPS and HAP (10:3:4.5) was less evident. This may be partly due to the fact that both systems were above their main transition temperature due to the high moisture content. At lower moisture contents, the T_g is higher, which agrees with the increase in stiffness/strength noted after conditioning at 33% RH.

Several factors may contribute to the increased stiffness and strength when the amylose content is increased. It has been suggested that a higher amount of amylose leads to a more entangled network which would contribute to the mechanical performance.[3] This could also account for the higher melt viscosity of the HAP material. Suggestions that amylopectin is more prone to degradation than amylose during processing may play a role in this context.[14] Residual crystalline structures or recrystalline structures associated with amylose could also account for the higher melt viscosity (and the improved mechanical performance) of the HAP material.[21] To complete the picture, it may be pointed out that since amylose has lower molecular mass than amylopectin, the higher melt viscosity of HAP is not primarily believed to associated with differences in molecular mass. The differences in molecular structure may however be a factor in this context.

The existence of a residual or recrystallized crystalline phase associated with amylose and with a rather high melting point, as indicated by thermal analysis, can thus, at least partly, explain the results obtained here.[21] From recorded diffractograms it is however difficult to ascertain whether such a crystalline structure exists in the present case. On the contrary, they are more indicative of a largely amorphous phase. A lower degree of crystallinity cannot however be ruled out since the limit for detection of a crystalline structure in materials of this kind has been estimated to be about 15%.[22] Even such a degree of crystallinity or lower can be expected to have an appreciable influence on the mechanical performance and the melt flow behavior. It may be remarked that Lourdin et al. could not detect any crystallinity using XRD in their glycerol-plasticized starch films containing different amounts of amylose.[21] They concluded that the observed differences in mechanical performance due to the amylose content could not be accounted for by crystallinity differences alone despite the high detection threshold of the technique. Apparently, the level of crystallinity and its importance with regard to the properties of plasticized and processed starch materials is still open to further study.

The higher melt viscosities mean that high-amylose materials are expected to be more difficult to process than NPS. However, by increasing the melt temperature from 140 to 160 °C, the melt viscosity of HAP 10:3:4.5 was reduced below the viscosity of NPS 10:3:4.5 at 140 °C. During the processing, residual opaque parts of material could be observed after the melt mixing step in the chamber mixer, but these disappeared after the molding step. Thus, in line with previous discussions, a higher melt temperature or a higher moisture content (since the melting point of amylose depends on the moisture content) may be required for the melt processing of HAP.[21] This must however be balanced against the possible onset of degradation of the material.

Both the moisture content during processing and the process temperature apparently had a significant influence on the mechanical properties of the NPS sheets. A similar behavior is also to be expected with HAP although it has not been studied here. A higher moisture content yields a lower melt viscosity which was here reflected in a lower film thickness. In principle, the same is to be expected if the process temperature is increased. This was not however observed within this work, probably because of an evaporation of moisture at the higher temperature. The important conclusion is that the moisture content of the thermoplastic starch must be carefully controlled in order to obtain the desired property profile.

Finally, the moisture sensitivity of the starch may to some extent restrict the application possibilities for these materials to situations where the humidity of the environment is rather low or to cases where the mechanical performance (and barrier properties) is sufficient at the expected humidity level (and variations in humidity). In principle, the usefulness of the thermoplastic starch materials at higher levels of humidity can be extended by chemical modification of the starch. This is however beyond the scope of this study.

The maximum in stiffness and strength of processed NPS at a process temperature of 140 °C may be the result of several factors. A low processing temperature may not give a complete melting (or sufficient softening) of the material. The melt temperature will also affect the orientation of the material, and the degree of orientation in the flow direction of the solidified material can be lower at a higher process temperature. It is well-known that the degree of orientation strongly influences the mechanical properties of polymers. Since the specimens were produced by compression molding, the degree of orientation is not however expected to be very pronounced. Another factor is that the starch materials are likely to be more prone to degradation at higher processing temperatures.

Conclusions

The main results can be summarized as follows:

After conditioning at 23 °C and 53% RH, the compression-molded glycerol-plasticized HAP exhibited a higher elastic modulus and a higher tensile strength than the corresponding NPS material, which is presumably a consequence of the higher T_g of the high-amylose material.

Parallel to the improvement in mechanical behavior, the HAP material exhibited a higher melt viscosity than thermoplastic NPS. Higher process temperatures may therefore be required for thermoplastic HAP materials.

A higher moisture content reduces the stiffness of the compression-molded starch materials and increases their ultimate elongation, due to a decrease in the T_g.

The process conditions during molding have a strong effect on the mechanical properties of thermoplastic NPS.

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