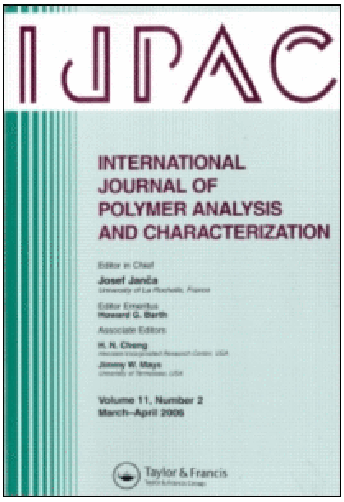

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On the Stress-Strain Behavior of Thermoplastic Starch Melts

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Abstract: Different grades of starch, glycerol, and water were blended in order to produce a series of thermoplastic starch materials. The starch grades used included native potato starch and modified grades of native potato starch, high amylose potato starch, and amylopectin potato starch. The modification of the latter three grades involved hydroxypropylation and oxidation. The main focus of the study was on the stress-strain properties or the drawability of the thermoplastic starch melts at 120° or 140°C. At these temperatures, the ultimate strain of the starch materials was found to be significantly lower than that of a high-density polyethylene reference at 180°C. In general, the strain at break of the melts based on the native potato starch and the modified native potato starch tended to increase when increasing the glycerol content (and the corresponding amount of water) but decreased as the melt temperature was increased from

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120° to 140°C. The chemical modification of the native potato starch appeared to promote the drawability of the melt.

Keywords: Melt extension; Rheology; Starch; Thermoplastic starch

INTRODUCTION

Materials based on starch have for a long time attracted considerable interest as a potential substitute for synthetic thermoplastics in certain applications.[1–4] The reason is that starch possesses a number of interesting properties or features: it has reasonably good mechanical properties and provides a good oxygen barrier in the dry state, is biodegradable and renewable, is available in large quantities, and does not rely on fossil resources. On the other hand, starch exhibits a number of drawbacks that limits its use in different situations: it is prone to thermal degradation at higher temperature, its resistance against water or moisture is rather poor with regard to mechanical performance and barrier properties, and it is not straightforward to process with conventional polymer processing techniques.

An obvious potential user of starch-based materials is the packaging industry, with the material in the form of a film. In some cases, starch can be applied as an aqueous solution to a substrate, and, after drying, a laminate is obtained. This is well known in the field of paper coating, and efficient manufacturing techniques are available for this purpose.[5,6] In other cases, a free film is required and one is then restricted to more conventional polymer processing methods like extrusion or film blowing. Here, the rheological properties and processability of thermally softened starch come into focus. In the available literature, there appears, however, to be a need for more detailed information with regard to extrusion processing and the associated rheological behavior of starch-based material.

In order to process starch with conventional techniques, the material has to be modified or plasticized. Melt-processed starch with a homogeneously distributed plasticizer, such as glycerol in combination with water, is commonly called thermoplastic starch, and its properties have been described in a number of research reports.[7–10] In the case of film processing, the drawability or the stress-strain properties of the melt are crucial. Very few reports have actually dealt with this processing aspect. The aim of this communication is to evaluate the stress-strain behavior of a rather typical thermoplastic potato starch material and indicate how it can be affected by the amount of plasticizer and processing temperature. In this context, the effect of modifying the starch on the drawability was also of interest. A comparison with the corresponding properties of a polyethylene melt is included.

MATERIALS AND METHODS

The starch used was a native potato starch (NPS), containing 21% amylose, kindly supplied by Lyckeby Stärkelsen (Kristianstad, Sweden). This grade was also used in a hydroxypropylated and oxidized form, denoted ONPS. An amylopectin grade (PAP) of potato starch, supplied by the same manufacturer, as well as a high amylose starch (HAP) supplied by Plant Science (Sweden) were also included. The latter material had, according to the supplier, an amylose content of approximately 86%. These two modified starches were here used only in hydroxypropylated and oxidized forms denoted OPAP and OHAP, respectively.

Glycerol (Rectapur from Prolabo, Sweden) was used as received as plasticizer for the starch. The NPS and ONPS starch grades were mixed with glycerol in two different weight proportions, starch:glycerol 100:30 (on a dry basis) and 100:45. In the case of OPAP and OHAP, the weight proportion was kept at 100:30.

The polyethylene used as a reference was a high-density polyethylene grade, Finathene® 6002 (Atofina, Belgium), with a density of 959 kg/m^3 and a melt flow index of 0.3 g/10 min (2.16 kg, ISO 1133).

Starch and glycerol were initially pre-mixed by hand. The water content of the mixture was then approximately 12 wt%. The blends were thereafter compounded in a co-kneading extruder (Buss PR 46, Switzerland, diameter $D = 46$ mm and length $L = 11D$) at a screw speed of 24 rpm. The compounding temperature was kept at 110°C for NPS and at about 95°C for the other combinations. The extruded strands were cut into pellets after leaving the die. With these extrusion conditions, the granular structure of the original starch material was more or less eliminated. However, it is possible that compounded material still contained some crystallites, although the degree of crystallinity is expected to be quite low.[11] The rheological experiments (described below) were performed at higher temperatures, and it was then expected, judging from their transparent appearance, that all melts were almost or completely amorphous.[11] This does not exclude the possibility that some minor residual crystallinity still was present in the melts, even at relatively high temperatures.

Before any measurements were carried out, the pellets were conditioned in a closed chamber containing a saturated solution of $Mg(NO_3)_2$ giving a relative humidity of 53%. The equilibrium water content of the compounded material was measured gravimetrically by heating the samples from 20° to 105°C in a Mettler M3 TG50 Thermobalance thermogravimetric analyzer (TGA) (Mettler Intrumente AG, Switzerland). The different compositions used are given in Table I. Note that an increase of the amount of glycerol was paralleled by an increase in the water content. The hydroxypropylation/oxidation treatment reduced

Table I. Compositions of the thermoplastic starch materials

Material	Glycerol (parts)	Water (wt%)
NPS 100:30	30	19
NPS 100:45	45	28
ONPS 100:30	30	15
ONPS 100:45	45	25
OPAP 100:30	30	14
OHAP 100:30	30	17

The amount of glycerol is given as parts (by weight) of the plasticizer per 100 parts of dry starch. The water content was determined after the conditioning.

the water content after conditioning somewhat, which to some extent is in agreement with the benefit of this kind of treatment with regard to water vapor permeability.[12]

The rheological properties of the thermoplastic melts were evaluated using a Rheoscope 1000 CEAST 6742/000 (Ceast SpA, Italy) capillary viscometer. When evaluating the shear viscosity as a function of the shear rate, three different capillaries were used. They had the same diameter, 1 mm, but different L/D-ratios: 5/1, 10/1, and 40/1, respectively. The viscosity measurements were carried out at 120° or 140°C (180°C in the case of polyethylene), and the measured data were subjected to the Rabinowitsch and Bagley corrections.

The rheoscope is also equipped with a rotating disc unit (positioned below the exit of the capillary) that picks up the extruded strand from the capillary, stretches it, and allows the stress-strain behavior of the melt to be determined. The strain in the strand was evaluated from the difference between the tangential velocity of the rotating disc and the velocity of the extruded strand at the exit of capillary, the latter being kept at 15 mm/s. During the experiments, the velocity of the rotating disc was linearly increased at a rate of $0.63\,\text{mm/s}^2$, thus stretching the extruded strand. The force required for extension of the melt was measured with a transducer. The initial temperature of the melts was kept the same as above, i.e., 120° or 140°C in the case of the thermoplastic starches. The stress-strain behavior of the polyethylene grade was determined at 180°C. Note that the stretching of the melt took place after the capillary and some cooling of the melt can be expected, i.e., the measurement is non-isothermal. This is, however, not expected to affect the main conclusions arrived at here. Typically, three to five rheological measurements were carried out for each material combination. The experimental scatter in the melt strength data was in most cases around 10% or lower. The measured values of strain at failure exhibited an appreciable scatter, which perhaps not is unexpected since the result is sensitive towards local disturbances. In the present case, onsets of foaming or slight degradation are examples of such disturbances. Typically the relative experimental scatter was of the order of 25% (expressed in relative terms), but in a few cases it could increase towards 50% or even higher.

RESULTS AND DISCUSSION

Figure 1 shows examples of shear viscosity as a function of shear rate for some of the thermoplastic starches after compounding in the co-kneading extruder. (the polyethylene was, however, not compounded.). The melt temperature was 140°C (for polyethylene 180°C), and the starch blends contained in this case 30 parts of glycerol. All materials exhibited a shear-thinning behavior. Hydropropylation and oxidation of the NPS obviously reduced the viscosity level appreciably, despite the somewhat lower water content. The same type of treatment of the HAP also appeared to reduce the viscosity level, when compared to previously reported results,[11] although OHAP still exhibited a relatively high viscosity level. The lowest viscosity at a given shear rate was here obtained with the OPAP grade. As reported earlier, a decrease in the melt temperature raised the viscosity whereas an increase in the glycerol content up to 45 parts reduced the flow resistance (here evaluated only for NPS

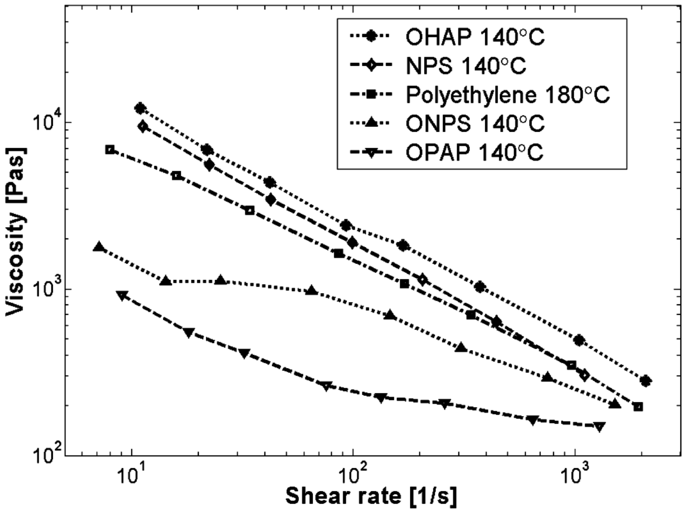

Figure 1. Viscosity as a function of shear rate at 140°C for some of the thermoplastic starch melts. The glycerol content was kept at 30 parts per 100 parts of starch (dry). The corresponding curve for the reference polyethylene at 180°C is also included.

Table II. Power law parameters K and n for some thermoplastic starch melts

Material	Temperature, °C	K, Pa s^n	n
NPS 100:30	120	173000	0.29
NPS 100:30	140	43600	0.32
ONPS 100:30	120	13600	0.51
ONPS 100:30	140	5600	0.56
OPAP 100:30	140	1660	0.64
OHAP 100:30	140	52300	0.33
Polyethylene	180	22900	0.39

and ONPS).[11] When the glycerol content increased, the water content also increased, which can contribute to the lower viscosity. Note that the polyethylene melt at 180°C exhibited viscosity levels that were somewhat lower than those of NPS and OHAP but higher than those of ONPS.

The shear rate ($\dot{\gamma}$) dependency of the viscosity (η) can with reasonable accuracy be described by a power law expression, i.e.:

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

where K is a constant (consistency) and n the flow exponent. Table II summarizes the values of K and n for some of the melts investigated here.

In addition to reducing the viscosity, an increase of the melt temperature increased the n-value in the case of NPS and ONPS; i.e., the melts exhibited a more Newtonian character. The hydroxypropylation/oxida-oxidation of NPS brings about a quite strong increase of the flow exponent, as shown in Table II.

Figure 2 shows the stress-strain curves (or more precisely the force-nominal strain curves) for NPS 100:30 and NPS 100:45 at 120°C and polyethylene at 180°C. These curves provide a measure of the drawability of the material after leaving an extrusion die. The most striking feature of this graph is the superior extensibility of the polyethylene melt (about 2000%) compared to the starch materials. The melt strength, expressed in terms of the force at rupture of the melts, was, however, higher for most of the thermoplastic starches. It may be remarked that the stress-strain measurements performed here do not indicate any strain-hardening behavior of the starch melts. Such a strain-hardening ability is sometimes considered to be important with regard to the processability of the melts, e.g., in conjunction with film blowing. A more detailed study is required in order to assess possible strain-hardening effects in thermoplastic starch melts, but this falls outside the scope of the present work.

Figure 3 shows the strain at break as a function of the content of glycerol for NPS and ONPS for the two temperatures used. Note that

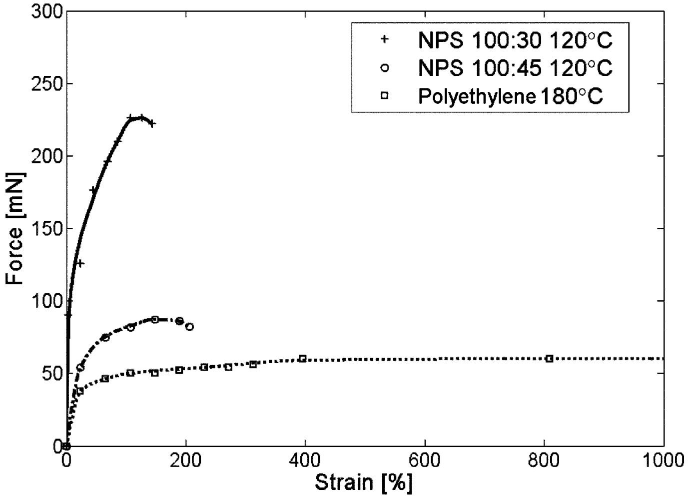

Figure 2. Force-strain curves for the thermoplastic starch melts NPS 100:30 and NPS 100:45 at 120°C and polyethylene at 180°C.

the water content increased as the amount of glycerol was raised. Increasing the amount of glycerol increased the drawability of the thermoplastic starch. This was especially pronounced in the case of the modified grade ONPS at 120°C. The corresponding effect for NPS was significantly more

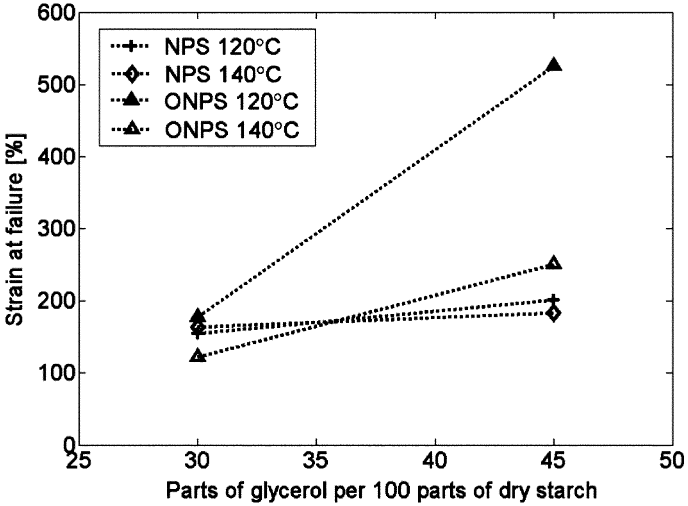

Figure 3. The strain at failure of NPS and ONPS as a function of the glycerol content at 120° and 140°C.

modest. Admittedly, the experimental scatter when measuring the extensibility of these materials was in some cases rather high, indicating that the results should be viewed upon with some caution. However, the general tendency was that higher amounts of glycerol and the chemical modification (hydroxypropylation/oxidation) improved the drawability of the NPS-based materials, whereas an increase of the melt temperature from 120° to 140°C reduced it. The latter observation refers mainly to ONPS; the change in extensibility was less clear in the case of NPS. The decrease in the drawability at the higher temperature could possibly be associated with onset of foaming and a slight degradation. The highest strain at break was here obtained with ONPS 100:45 at a temperature of 120°C (of the order of 500%). The corresponding melt strength was highest for the NPS material and it decreased for both NPS and ONPS with increasing glycerol content and melt temperature (in most cases).

The results from the stress-strain measurements of the melts are summarized in Table III.

The melt strengths of the melts based on the modified starches OPAP and OHAP were in general somewhat lower than that of ONPS 100:30, whereas the strain at rupture was in the same range or higher than the corresponding value for the ONPS 100:30. The melt strength and the strain at break decreased with increasing temperature for OHAP, which parallels the behavior of the materials based on natural starch (it may be noted that at 140°C, the strain at failure of OHAP displayed an appreciable scatter, which might be associated with onset of foaming/degradation). OPAP, on the hand, exhibited a marked increase in the strain at failure when the temperature was increased up to 140°C. The reason for this is not clear at present.

Table III. Melt strength and strain at break for the investigated melts

Material	Temperature, °C	Melt strength, mN	Strain at break, %
NPS 100:30	120	220	155
NPS 100:30	140	136	165
NPS 100:45	120	87	200
NPS 100:45	140	68	180
ONPS 100:30	120	122	180
ONPS 100:30	140	90	120
ONPS 100:45	120	46	525
ONPS 100:45	140	47	250
OPAP 100:30	120	57	165
OPAP 100:30	140	68	360
OHAP 100:30	120	86	230
OHAP 100:30	140	51	175
Polyethylene	180	46	≈2000

FINAL REMARKS

It is clear that there is a great difference in extensibility between the high-density polyethylene reference and the thermoplastic starches. It was found to be appreciably lower in case of the latter materials, which can be expected to lead to difficulties when drawing down films or applying film blowing. The situation is to some extent improved when increasing the amount of added glycerol (and thus water), but still the drawability is far from that of polyethylene. This implies that when producing starch films further modifications of the material can be required or that the processing technique must be adapted to the material properties. An obvious first extension of the above study would be to increase the amount of added glycerol in the OPAP- and OHAP-based materials, since these materials exhibited rather interesting extension properties already at a glycerol content of 30 parts. However, there is clearly room and need for additional studies with regard to the processing of starch-based polymeric systems. As an illustration of this, it may be mentioned that in a preliminary study, the compounded NPS 100:45 was further processed in a single-screw extruder. This additional extrusion improved to some extent the drawability (strain at break) of the melt.

At this stage it is quite difficult to speculate about the reasons for the difference in stress-strain behavior between the starch materials and the polyethylene grade and why hydroxypropylation/oxidation appears to have a positive effect on mechanical performance. A more detailed study to address those issues is planned. In general, however, the difference in drawability between the thermoplastic starches and the polyethylene reference is to be associated with the molecular structure of the melt and how the macromolecules respond to external stress fields. In order to improve the processing properties of starch, a more thorough characterization of the starch material is required, and this might warrant developments of new or modified characterization techniques. Furthermore, a better understanding of the mechanisms underlying the conformational changes of the starch molecule when subjected to flow fields is required.

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