ELSEVIER

Thermoplastic starch–lignosulfonate blends. 1. Factorial planning as a tool for elucidating new data from high performance size-exclusion chromatography and mechanical tests

L.C. Morais, A.A.S. Curvelo*, M.D. Zambon

Instituto de Química de São Carlos, Universidade de São Paulo, CP 780, São Carlos, SP 13560-750, Brazil

Abstract

Blends of cornstarch, glycerol and lignosulfonate were prepared in variable-speed batch mixer at 150–160 °C, with the glycerol in various proportions from 20 to 40% and lignosulfonate from 10 to 40%. Alterations in HPSEC chromatogram profiles after the thermal processing were analyzed.

The results showed that an increase in glycerol preserves the starch chains from degradation, which occurs to a smaller extent in samples without both lignosulfonate and modified lignosulfonate.

Researchers have attributed the degradation of the starch compounds to shear-induced fragmentation, which increases the viscosity of the starch–glycerol matrices. Applying factorial planning at two levels, it was possible to obtain equations that better represent the effects caused by the presence of glycerol and lignosulfonate in the thermoplastic matrices.

The effect of using hydroxymethylated lignosulfonate on the mechanical properties of starch was also investigated.
© 2005 Elsevier Ltd. All rights reserved.

Keywords: Thermoplastic starch; Lignosulfonate; Blends; HPSEC; Mechanical essays

1. Introduction

In recent years, the study of new materials manufactured from the biomass has received attention in various research areas. The main objective of this research is to replace some synthetic plastics with biomaterials that combine good mechanical properties with a short lifetime, potentially yielding a substantial positive impact on the environment. An important earlier survey (Beach, Boyd, & Uri, 1995) revealed the positive effect of the use of biodegradable polymer resin on the U.S. economy.

Polysaccharides, and specially starch and its derivatives, have been studied extensively to this end. Starch is a polymer of glycosidic units linked by α-(1–4) bonds. It is composed of two polymers, amylose and amylopectin (Coultate, 1996; Whistler, Bemiller, & Paschall, 1984).

The first has a linear conformation and an average molecular mass of around 10^5 g mol^{-1}. The second is a branched structure that has an average molecular mass of around 10^6–10^7 g mol^{-1} (Chen, Fringant, & Rinaudo, 1997). Starch is formed in granules, which exhibit molecular ordering and a crystalline X-ray diffraction pattern. When heated in suitable conditions, the granules lose their shape and develop an amorphous phase (Jarowenko, 1977). When plasticizers are added to this amorphous phase, thermoplastic starch is produced (TPS) (Wiedmann, & Strobel, 1991). Under these conditions, a great variety of composites and blends can be produced.

The substances that compose starch are liable to suffer changes in their structure during processing, caused by shear-induced fragmentation. These changes are generally measured by techniques such as high-performance size-exclusion chromatography (HPSEC), light scattering, viscometry and so on. Some authors (Chen et al., 1997; Millard, Wolf, Dintzis, & Willet, 1999; Young, 1984) have shown that there are discrepancies among the average molecular weight values obtained for starch samples that were prepared by different methods. Knowledge of the extent of

* Corresponding author. Tel.: +55 162 739 938; fax: +55 162 739 952.
 E-mail address: aprigio@iqsc.usp.br (A.A.S. Curvelo).

these changes is very important as they affect the properties of composites or blends (Carvalho, Curvelo, Zambon, & Gandini, 2003; St-Pierre, Favis, Ramsay, Ramsay, & Verhoogt, 1997; Willet, Millard, & Jasberg, 1997). However, there is still a lack of data concerning the molecular weight distribution of starch after it has been processed in the presence of lignin or its derivatives.

The use of lignin as a filler in materials based on starch or synthetic polymer has been reported in several articles (Baumberger, Lapierre, Monties, Loudin, & Colonna, 1997; Baumberger, Lapierre, & Monties, 1998; Baumberger, Monties, & Valle, 1998; Tudorachi, Rusu, Cascaval, Contantin, & Ruginã, 2000). Advantageous features such as its chemical composition (rich in phenolics), purchase price and abundance have made lignin a material of choice, with enormous potential, for use in the preparation of new plastic materials. In a study of lignin added to synthetic polymers during extrusion, it showed good stabilizing properties against heat and light, when low concentrations were employed (Alexy, Kosíková, & Podstránska, 2000). The presence of phenolic units confers an antioxidant property; probably enhances its mechanical properties during the extrusion or increase the degradation rate of the polymers.

In the work reported here, we produced thermoplastic starch–sodium lignosulfonate blends using glycerol as the plasticizer. The materials obtained had their molecular weight distribution and stress–strain relationships studied accordance with a 2^2 factorial design. Hydroxymetylated lignosulfonate was prepared, and subjected to the same tests, in thermoplastic blends containing the same proportions of lignosulfonate.

2. Experimental

2.1. Materials

Corn Products (Brazil) and Melbar (Brazil) provided regular cornstarch 'Amidex 3001' ($\sim 28\%$ amylose) and sodium lignosulfonate (LS), respectively. The plasticizer (high quality glycerol) was purchased from Sigma. The pure amylose was obtained by precipitation of starch with *n*-butanol, after the starch is heated up to 90 °C.

2.2. Preparation of thermoplastic starch–lignin blends

Before the blending was carried out, the starch, glycerol and lignosulfonate were mixed in plastic bags and water was added to make the total weight of liquid up to 50% in weight of the dry starch, i.e. glycerol, water content of starch and water added. The water was included only as a processing agent, since it escapes from the mixture at the high temperatures used in the unsealed process. About 0.5% by weight of stearic acid was added to the mixture. An amount of each mixture was put in a Haake Rheomix 600 batch

mixer equipped with roller rotors and software to register the torque profile curve. The temperature of the pre-heated mixing chamber was kept at 160 °C and the rotors operated at 50 rpm for a total experimental time of 6 min. The amount of lignosulfonate is expressed relative to the total weight of the mixture, i.e. the sum of starch (A), glycerol (G) and lignosulfonate (LS). The weights of glycerol and starch are expressed as percentages of the matrix (A plus G, before the LS is added). The amount of glycerol was calculated in terms of the starch dry weight. This method was used for simplicity, since the various matrices have constant ratios of glycerol and starch. The resulting mixtures of Amidex 3001 and glycerol are thermoplastic matrices, denominated A70G30, A60G40 and A80G20. When LS is present, for example, at 10% of total weight in an A60G40 matrix, the mixture is labelled A60G40LS10 and so on.

2.3. Hydroxymethylation of lignosulfonate

The lignosulfonate (LS) was reacted with formaldehyde in accordance with the method described previously (Peng, Riedl, & Barry, 1993).

46.65 g of lignin were dissolved in 103.9 g of sodium hydroxide solution (6.69%) and kept at 80 °C for 90 min on stirring. $NaHCO_3$ was added to maintain the pH around 10.5. After this, 19.5 g of formaldehyde solution (38.5%) was added and the mixture was stirred constantly for 90 min. After the reaction is completed, the samples were brought to pH ~ 5.0 with 0.25 M HCl solution and then centrifuged at a rate of 3500 rpm for 15 min and washed until the pH was ~ 7.0.

2.4. Stress–strain essays

The stress–strain assays were based on ASTM D638M standard method. An Instron machine 5500R model with a cell charge of 500 kgf was used. The speed of test was 50 mm min^{-1} and for each sample five replicates were done. The samples were previously conditioned in 54% of environmental relative humidity. The values for yield stress and strain at rupture were considered.

2.5. High performance-size exclusion chromatography (HPSEC)

The starch in the blends were analyzed in a SCL-10A Shimadzu HPSEC Chromatograph, equipped with an LC-10AD pump, CTO-10A oven temperature controller and RID-6A refractive index detector. The calculations of $\overline{Mz}$, $\overline{Mw}$ and $\overline{Mn}$ were made using a HPSEC software for the CLASS-LC10. The columns used for HPSEC separation were the Ultrahydrogel pre-column (purchased from Waters), plus three linear Ultrahydrogel columns arranged in series (7.8 mm i.d. $\times$ 30 mm). The eluent phase was a 0.1 M $NaNO_3$ solution whose pH was adjusted to ~ 11.5.

An ultrasonic cleaning bath degassed the eluent, which was filtered through a 0.45 μm glass fiber filter. The elution flow was 0.8 mL min^{-1} and the pressure 30 kgf cm^{-2}.

The samples were stirred in 1 M NaOH solutions and subsequently filtered through in a paper filter (1 μm of porous diameter) and then through glass fiber filter (same porous size). The thermoplastic samples dissolved readily and completely. Only the starch sample (Amidex 3001) was heated to 80 °C in 1 M NaOH solution to guarantee total solubility. Despite the high viscosity of the solution of Amidex 3001 starch, the solution obtained was clear, with no evidence of dispersed particles.

The concentration of the samples was 10 mg mL^{-1} and the injection volume was 20 μL. The standards used were derived from Pulullan (polymaltotriose from Polymer Laboratories Ltd), which have average molecular masses of 62; 180; 738; 5800; 12,200; 23,700; 48,000; 100,000; 212,000; 380,000 and 1,600,000.

3. Results and discussion

Prior to the discussion of the results some points should be clarified.

In the chromatograms, the intensity of signals (RI signals) were normalized against the highest intensity between 20 and 33 min elution time and, in the integration of peak areas, the signals after 33 min were ignored in the molecular weight calculations. However, these signals remain in the chromatograms because they are result from processing conditions.

3.1. Chromatograms

A third-order polynomial curve was fitted to the Pulullan data, allowing more precise calculation of the largest regular cornstarch fraction, which has a portion beyond the range of the Pulullan data.

Fig. 1 shows the chromatograms for Amidex 3001 and its corresponding extracted amylose fraction.

For Amidex 3001, the two main peaks confirm the presence of two components, amylose and amylopectin. The latter can be identified firstly by its large molecular mass than that of amylose, and secondly, its fraction in the starch, which is about 72% against ∼28% of the amylose. The smaller fractions that appear between 33 and 36 min are residual fragments of polysaccharides, having average molecular masses around 2000 g mol^{-1}, based on the calibration curve.

The curve obtained with purified amylose shows a small fraction around 22 min, which corresponds to residual amylopectin, whereas the larger fraction of purified amylose is distributed in the region of the shoulder observed in the Amidex 3001 curve. To this sample, practically no signals were observed between 35 and 36 min, since this fraction
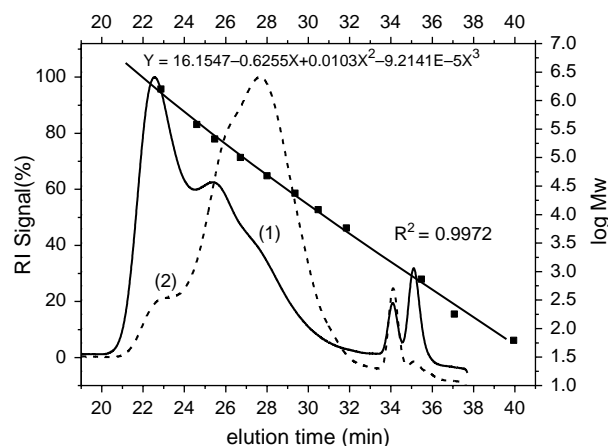

Fig. 1. Chromatograms of HPSEC for Amidex 3001 (1) and Amylose purified (2). Third order polynomial equation of fitting for standards of Pulullan.

has a molecular mass that did not allow its precipitation with *n*-butanol.

The average molecular masses for native starch, purified amylose and processed samples are given in Table 1.

The polydispersity ($\overline{Mw}/\overline{Mn}$) found for Amidex 3001 is larger than that for amylose because of the precipitation process, which leads to fractionation.

Fig. 2 shows the chromatograms obtained for different starch–glycerol matrices after thermal processing. The chromatogram of Amidex 3001 is shown to facilitate the visualization of the changes in the chromatogram profiles.

Comparison of the chromatogram of Amidex 3001 with those of the processed samples allows us to see that the region of the shoulder between 24 and 26 min was strongly affected by the processing. There was a significant decrease in the fraction corresponding to shoulder, as the amount of glycerol decreased. This confirms the use of glycerol as plasticizer, which diminishes the shear-induced cleavage of macromolecules by decreasing the viscosity. Some authors have reported the action of water (Mercier, 1977) or glycerol (Willet et al., 1997) in decreasing of the starch degradation. In another study, Forssell, Mikkilä, Moates, and Parker, (1997) worked with similar amounts of water and glycerol to those used here, and their results for $\overline{Mw}$ and $\overline{Mn}$ followed a similar trend to this work, i.e. a decrease in glycerol caused an increase in degradation. However, the chromatographic profiles found by Forssell et al. (1997) showed broader signals than that found by us, which can be attributed to the processing conditions.

Both $\overline{Mw}$ and $\overline{Mn}$ values for these samples were slightly larger than for Amidex 3001 (Table 1), indicating that the mixing process affected the amylose fraction more strongly than the amylopectin fraction. It can be seen that, the position of the main peak is unaffected, although its profile has become narrower.

The torque values for samples were recorded during processing and found to be 12, 25 and 51 N m for A60G40,

Table 1
Average values of the experimental results obtained from different techniques that were employed to characterize the blends

Samples	Stress (MPa)	Strain (%)	Young's modulus (MPa)	$\overline{Mz}$ ($\times 10^6$) g mol^{-1}	$\overline{Mw}$ ($\times 10^6$) g mol^{-1}	$\overline{Mn}$ ($\times 10^5$) g mol^{-1}	$\overline{Mw}/\overline{Mn}$
Amidex 3001	–	–	–	3.79	1.24	1.51	8.2
Amylose purified	–	–	–	2.08	0.29	0.60	4.8
A60G40	1.4	16	16	3.91	1.37	1.64	8.3
A70G30	3.7	34	50	3.28	1.38	2.27	6.1
A80G20	8.7	22	466	3.14	1.43	2.62	5.5
A60G40LS10	1.2	20	12	3.43	1.27	1.43	8.9
A60G40LS40	0.5	75	10	2.61	0.61	0.67	9.1
A70G30LS25	1.0	93	11	2.92	0.94	0.95	9.9
A80G20LS10	4.4	24	137	2.33	0.88	0.71	12.4
A80G20LS40	4.2	56	195	2.76	0.74	0.73	10.1
A60G40LSM10	0.6	56	3	1.91	0.59	1.08	5.5
A60G40LSM40	0.9	57	7	1.77	0.41	0.65	6.3
A70G30LSM25	1.6	80	16	1.33	0.37	0.76	4.9
A80G20LSM10	5.6	40	189	1.86	0.53	1.06	5.0
A80G20LSM40	2.4	54	46	1.31	0.35	0.78	4.5

A70G30 and A80G20, respectively, showing that exist a correlation between amount of glycerol and resistance of the paste, i.e. the torque values are reduced by an increase in glycerol content.

Sodium lignosulfonate was also included in various amounts in the blends, so as to follow the changes in chromatographic profiles when different ratios of A–G–LS were used, as shown in Fig. 3.

Although lignin can act as an antioxidant (Alexy et al., 2000), Fig. 3 shows that increased lignin caused a decrease in molecular mass, indicated by the shifts in the peak positions to longer elution time. The values obtained for average molecular masses (Table 1) confirm this observation.

The sample A60G40LS10 showed a chromatographic profile similar to that of the A60G40 matrix (without LS). Although the same quantity of LS (10%) is present in the sample A80G20LS10, for this latter was observed a displacement of peak to longer elution time. This is another support that the amount of glycerol is important to reduce the degradation effect.

The sample A70G30LS25 showed a broader chromatographic profile than the A60G40LS10 sample, which has a higher amount of glycerol. The sample exhibited intermediary values for $\overline{Mz}$, $\overline{Mw}$, $\overline{Mn}$ and polydispersity (Fig. 3).

Samples having 40% of LS showed similar chromatographic profiles, but the region between 24 and 33 min exhibited an increase in signal intensities, which are almost strong as the initial peaks. The peaks around 34 min also show increases in the signal intensity when the amount of LS is increases, thus, these peaks cannot be attributed exclusively to the starch fraction, because the LS may contribute to the signals.

Alexy et al. (2000) studied the effect of lignin in blends with polyethylene and polypropylene, and concluded that an increasing in lignin concentration produces an increase in the melt flow index, which contributes to degradation.

Samples of LS were submitted to the reaction of hydroxymethylation (yielding LSM) and the changes in molecular weight distributions in the corresponding starch
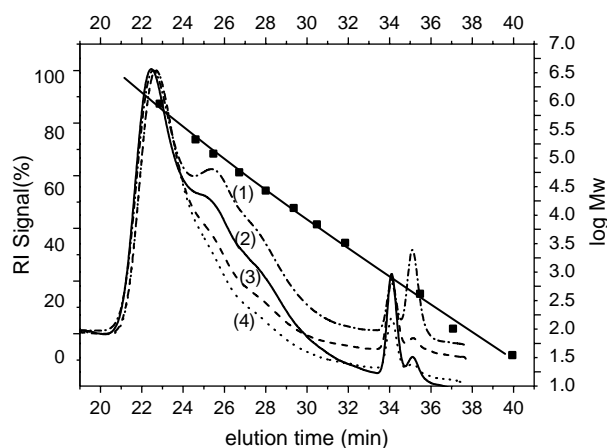

Fig. 2. Chromatograms of HPSEC for Amidex 3001 (1), A60G40 (2), A70G30 (3) and A80G20 (4).
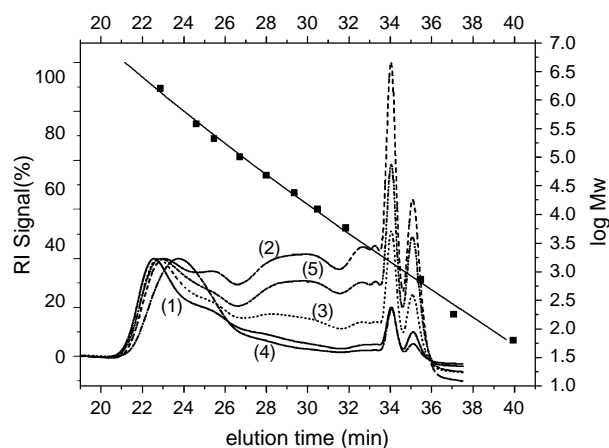

Fig. 3. Chromatograms of HPSEC for A60G40LS10 (1), A60G40LS40 (2), A70G30LS25 (3), A80G20LS10 (4) and A80G20LS40 (5).
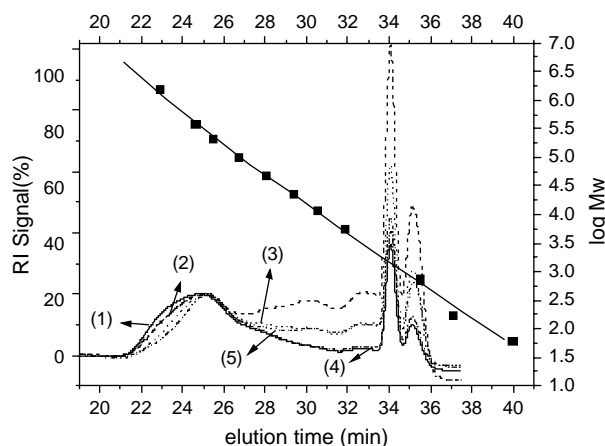
Fig. 4. Chromatograms of HPSEC for A60G40LSM10 (1), A60G40LSM40 (2), A70G30LSM25 (3), A80G20LSM10 (4) and A80G20LSM40 (5).

blends were also studied, the chromatograms being shown in Fig. 4 and the average molecular masses in Table 1.

The chromatograms for LSM samples had peaks displaced to longer elution times than LS samples. In Table 1 it can be seen that the average molecular masses for LSM samples are smaller than for LS samples.

Samples having 10% of LSM showed similar chromatographic profiles, suggesting that the glycerin was not so effective in decreasing the degradation caused by shearing. The same was observed for both samples A70G30LSM25 and A80G20LSM40.

Although the hydroxymethylic groups are attached to the structure of the lignosulfonate as side groups, it is most probable that during the heating step cross-linking occurs, which would increase the viscosity.

Two observations are consistent with this. Firstly, after dissolving the samples in preparation for HPSEC analysis, a resistant part of the LSM was seen to remain insoluble. The hypothetical cross-linking can occur between lignin–lignin or lignin–starch chains. The second point arises from analysis of the recorded values of the torque, which are coherence with the variations of starch degradation as a function of LSM content. Thus for A60G40LSM10 and A60G40LSM40, the torques were 13 and 17 N m, respectively, while A80G20LSM10 and A80G20LSM40 gave torques of 26 and 49 N m, respectively.

Despite the ratio of starch–glycerol is kept constant for each set of the samples, the LSM amount makes the difference for the torque values. From Table 1 is seen that in the presence of the LSM the molar mass of the starch is considerable decreased, this implies in a decrease of viscosity and finally in the torque. It allows us conclude that there is a good interaction between LSM and thermoplastic matrix.

These values also show that when 40% of glycerol was used, the torque varied slightly, showing that in these conditions the viscosity was almost unaffected by LSM. In contrast, with 20% glycerol, the torque was increased

Table 2
Experimental factorial design 2^2 with lower ($-$) and upper ($+$) levels for glycerol and lignosulfonate (L) contents

Experiments	Variable levels	
	Glycerol (G)	Lignosulfonate (LS)
A60G40L10	+	−
A60G40L40	+	+
A70G30L25	0	0
A80G20L10	−	−
A80G20L40	−	+

The signal 'L' identifies both lignosulfonates, LS and LSM.

almost two-fold by the rise in LSM. The values of $\overline{Mz}$, $\overline{Mw}$ and $\overline{Mn}$ given in Table 1 corroborate these findings.

3.2. Factorial planning

To evaluate the extent of the effects caused by glycerol and amount of lignin (LS or LSM) on the samples, the interaction effects that may occur between the variables and to attempt to predict these effects on the physical properties, we applied factorial planning at two levels (Table 2).

3.3. Effects studied in lignosulfonate blends

The values obtained for stress, strain, $\overline{Mz}$, $\overline{Mw}$ and $\overline{Mn}$ were analyzed as functions of glycerol and lignosulfonate contents in starch blends by factorial planning at two levels. The data for p-level (95% confidence), estimated effect, standard error, r-squared and Student's t parameter are shown in Table 3.

The results for $\overline{Mz}$, $\overline{Mw}$ and $\overline{Mn}$ that were analyzed by HPSEC that had p-values upper 0.10 (90% confidence) obtained from factorial planning will be not considered.

The criterion used to decide if the effects are significantly different from zero consists in taking the value of Student's t, which depends on the degree of freedom, and multiplying it by the standard error. If the estimated effect value is larger than the absolute value of this calculation, then it should be taken as significant. The values of r-squared and p-level are also relevant statistical data that need to be checked together.

Tables 3–6 show each response analyzed with the corresponding values of the estimated effects for $\overline{Mz}$, $\overline{Mw}$, $\overline{Mn}$, stress and strain.

The interaction effects had significant values for $\overline{Mz}$, $\overline{Mw}$ and $\overline{Mn}$ p-levels. This means that the main effects need to be analyzed together. The r-squared value corroborate for this, as it defines whether the equation will fit well to the data, allowing a good prediction. The differences in responses between the upper and lower levels for both variables give us a perfect idea of what is happens when we move from -1 to $+1$ factor.

Although the variable LS has a large value for the $\overline{Mz}$ p-level, the effect of interaction between G and LS is also relevant. The situation is analogous for $\overline{Mw}$ and $\overline{Mn}$, which

Table 3
Statistical results for $\overline{Mz}$, $\overline{Mw}$ and $\overline{Mn}$ with their respective estimated effects obtained from statistical treatment

	Estimated effect	Standard error (±)	Estimated regression coefficient	*p*-level	*r*-squared[a]
Mz					
Average[b]	2.866×10^6	25,826	2.866×10^6	–	0.9948
Glycerol	335,000	57,749	167,500	0.1120	
LS	−55,000	57,749	−27,500	0.3574	
Interaction	−765,000	57,749	−382,500	0.0495	
Mw					
Average[b]	900,000	20,000	900,000	–	0.9914
Glycerol	100,000	44,721	50,000	0.2639	
LS	−370,000	44,721	−185,000	0.0755	
Interaction	−290,000	44,721	−145,000	0.0961	
Mn					
Average[b]	90,200	2400	90,200	–	0.9927
Glycerol	32,000	5366	16,000	0.1043	
LS	−36,000	5366	−18,000	0.0929	
Interaction	−40,000	5366	−20,000	0.0838	

Variables are glycerol and LS.
[a] Linear coefficient of the statistical equations.
[b] *r*-squared means how good predicted and experimental are fitted.

have large values for the glycerol variable. Thus, we can use the values from Table 3 for the estimated regression coefficient to obtain the following normalized equations:

$$\overline{Mz} = 2.866 \times 10^6 + 1.675 \times 10^5 \times G - 2.75 \times 10^4 \times LS$$
$$- 3.825 \times 10^5 \times G \times LS$$

$$\overline{Mw} = 9.0 \times 10^5 + 5.0 \times 10^4 \times G - 1.85 \times 10^5 \times LS$$
$$- 1.45 \times 10^5 \times G \times LS$$

$$\overline{Mn} = 9.02 \times 10^4 + 1.6 \times 10^4 \times G - 1.8 \times 10^4 \times LS$$
$$- 2.0 \times 10^4 \times G \times LS$$

Table 4
Statistical results for stress and strain with their respective estimated effects obtained from statistical treatment

	Estimated effect	Standard error (±)	Estimated regression coefficient	*p*-level	*r*-squared
Stress					
Average	2.19	0.0344	2.19	–	0.8396
Glycerol	−3.17	0.0769	−1.58	<0.0001	
LS	−0.28	0.0769	−0.14	0.0015	
Interaction	−0.45	0.0769	−0.22	<0.0001	
Strain					
Average	55.8	1.4377	55.8	–	0.4836
Glycerol	3.90	3.2148	1.95	0.2392	
LS	38.4	3.2148	19.2	0.0001	
Interaction	15.3	3.2148	7.6	<0.0001	

Variables are Glycerol and LS.

The signals $+$ and $-$ in the equations indicate positive and negative effects of the variable over the responses, respectively, and the first value (the intercept) in each equation represents the average value. LS variable has a negative coefficient in each equation, signifying that its action contributes to the degradation of starch chains. In contrast, the glycerol (G) variable acts in the opposite sense. The interaction effect (G×LS) has a large coefficient and it plays an important role when the level is moved from -1 to $+1$, as it depends on the combined action between G and LS. While the glycerol effect is responsible for the plasticizing effect that decreases shear-induced degradation, LS being miscible with glycerol, can remove it from the plasticized starch chains and increases the viscosity of the mixture. Moreover, rupture of starch chains occurs which is verified by the broadening of the chromatograms (Fig. 3).

The responses for stress and strain were also analyzed by factorial planning at two levels, as discussed above, the results, shown in Table 4, exhibit small *p*-level values for their interaction effects.

Five measurements were made for each response, allowing the criterion described above, that defines which variables are important, to be applied. From Table 4, we can conclude that the glycerol variable can be neglected in the equation for strain (poor *p*-level value). This suggests that the response for strain will not be predicted well in terms of G, and analyzing the *r*-squared value the LS can also be neglected. Perhaps another variable that was not analyzed would play an important role in the strain response.

For example, before the samples were assayed in an Instron machine, they were subjected to conditioning in an environmental of relative humidity 54%, in accordance with ASTM D638 M. This suggests that the presence of water

Table 5
Statistical results for $\overline{Mz}$, $\overline{Mw}$ and $\overline{Mn}$ with their respective estimated effects obtained from statistical treatment

	Estimated effect	Standard error ($\pm$)	Estimated regression coefficient	p-level	r-squared
Mz					
Average	1.636×10^6	153,000	1.636×10^6	–	0.6589
Glycerol	255,000	342,118	127,500	0.5986	
LSM	$-345,000$	342,118	$-172,500$	0.4889	
Interaction	205,000	342,118	102,500	0.6614	
Mw					
Average	450,000	40,000	450,000	–	0.7364
Glycerol	60,000	89,442	30,000	–	
LSM	$-180,000$	89,442	$-90,000$	0.0628	
Interaction	–	89,442	–		
Mn					
Average	86,600	5300	86,600	–	0.8474
Glycerol	-5500	11,851	-2750	–	
LSM	$-35,500$	11,851	$-17,750$	0.0266	
Interaction	-7500	11,851	-3750	–	

Variables are Glycerol and LSM.

affected the strain response more strongly than that for stress response, because it acts as plasticizer for polymer chains.

For stress response, the results from Table 4 allow us to obtain a normalized expression:

$$\text{Stress} = 2.190 - 1.584 \times G - 0.141 \times LS - 0.225 \times G \times LS$$

This equation shows that the effects of variables G and LS are to reduce the stress, i.e. the strength of the sample. It accords with the fact that A–G matrices without LS exhibited values for stress larger than those with LS, and shows that LS and G can act together as plasticizer of starch chains, breaking the interactions between the starch chains and allowing a sliding of one chain over the others. Baumberger, Lapierre, et al. (1998) and Baumberger, Monties, et al. (1998) studied the effect of molecular mass of the lignin on mechanical properties of starch–lignin blends and concluded that, when small molecular mass particles as present they act as plasticizer of the starch chains. The coefficient for G is about eleven and seven times larger than that for LS and for G–LS interaction,

respectively, which shows that, going from the upper to lower level, the stress tends to increase, as expected.

3.4. Effects studied in hydroxymethylated lignosulfonate blends

Blends prepared from lignosulfonate chemically modified had their average molar masses and mechanical properties estimated by using factorial planning. The results are shown in Tables 5 and 6.

The only response for $\overline{Mz}$ had large p-level value, despite the r-squared was good (0.9948), statistical corrections cannot to be applied for p-level, making it impossible to obtain a model for prediction. Applying p-level corrections for both $\overline{Mw}$ and $\overline{Mn}$, the results are improved and normalized equations were obtained as follow:

$$\overline{Mw} = 4.5 \times 10^5 - 9.0 \times 10^4 \times LSM$$

$$\overline{Mn} = 8.66 \times 10^4 - 1775 \times 10^4 \times LSM$$

These equations mean that the presence of LSM has a deleterious effect on the starch chains in the thermoplastic matrices. Analyzing the values for $\overline{Mz}$, $\overline{Mw}$ and $\overline{Mn}$ in Table 1 it is possible to verify that a great decrease in these average molecular masses occurs as the amount of LSM increases.

By taking the estimated effects into account, it is possible to predict the average molecular masses of these blends from the equations above. Under these conditions, we can affirm that an increase in amount of LSM will decrease the average molecular mass. Both equations above show that the presence of LSM is the responsible variable by decreasing observed, which suggests that the chemical modification in LS is the main responsible for the changes in starch structure.

Table 6
Statistical results for stress and strain with their respective estimated effects obtained from statistical treatment

	Estimated effect	Standard error ($\pm$)	Estimated regression coefficient	p-level	r-squared
Stress					
Average	2.20	0.0494	2.20	–	0.9567
Glycerol	-3.25	0.1104	-1.62	<0.0001	
LSM	-1.45	0.1104	-0.72	<0.0001	
Interaction	1.71	0.1104	0.86	<0.0001	
Strain					
Average	57.4	1.0136	57.42	–	0.1936
Glycerol	9.32	2.2664	4.66	0.0005	
LSM	7.24	2.2664	3.62	0.0045	
Interaction	-6.41	2.2664	-3.21	0.0103	

Variables are Glycerol and LSM.

When the stress–strain properties were analyzed, as noted above for LS blends, prediction of the strain response by this method was discarded, despite the small *p*-levels and standard errors, because the *r*-squared value showed a poor correlation between the experimental and predicted values (Table 6).

Therefore, this response should be disregard, supporting the hypothesis about the existence of an unconsidered variable that affects the strain.

Using the estimated regression coefficients in Table 6, the normalized equation for stress is:

$$\text{Stress} = 2.2052 - 1.623 \times G - 0.724 \times LSM + 0.856 \times G \times LSM$$

As expected, the individual variables, G and LSM, act in the sense of decreasing the stress, as discussed formerly. On the other hand, the interaction effect (G×LSM) is significant and tends to increase the stress, when the variables G and LS are both at their upper or lower levels. When LS or LSM is mixed with glycerol alone, the material produced is weak and its strength depends on the concentration of glycerol. The material changed from soft to brittle, as glycerol concentration was decreased, but it was not possible to prepare material suitable for assay. However, this information indicates the probable existence of domains rich in glycerol–LS, which could contribute to the effects that were observed.

The existence of different phases is being investigated by dynamic mechanical analysis, since differential scanning calorimetry gives no information on this question.

4. Conclusions

HPSEC analysis was performed on native starch, purified amylose and samples obtained after the thermal processing, to reveal the differences in their chromatographic profiles. It was found that the conditions used to produce thermoplastic starch damage the starch structure. The presence of glycerol and water decrease considerably the degradation, seen in slight changes in chromatographic profiles in the region of lower elution time.

An increase in LS content causes increase in degradation of the starch chains, according to the changes in the chromatographic profiles, as confirmed by the average molecular masses. LS can extract glycerol from starch chains, increasing the shear-induced degradation.

When LSM was used, degradation of the starch structure was also observed but in this case, the most probable hypothesis is the possible occurrence of cross-linking between hydroxymethylated lignin with polymeric structures during thermal processing.

The use of factorial planning allowed us to obtain equations based on statistical criteria, which can be used to predict some of the properties of starch–lignosulfonate blends.

For the LS variable, one interesting result consists in the existence of interaction effects between glycerol and LS, which offer a better understanding of the blend properties. The signals (+and −) in the equations showed that the main effect of LS is to increase degradation of starch chains, while the glycerol opposes this effect and preserves them. It was possible to predict the stress response, whereas, it was not possible in the case of strain, perhaps other variables could be used to predict this property.

For LSM blends, the equations confirmed our suppositions, given that only the LSM variable was relevant to the prediction of $\overline{Mw}$ and $\overline{Mn}$. As for LS blends, the stress responses for these blends are negatively influenced by the variables, LSM and glycerol (G), when they are used at their upper levels.

It was not possible to predict the strain response corroborating the observation mentioned for LS blends.

Acknowledgements

References

Alexy, P., Kosíková, B., & Podstránska, G. (2000). The effect of blending lignin with polyethylene and polypropylene on physical properties. *Polymer*, *41*, 4901–4908.

Baumberger, S., Lapierre, C., & Monties, B. (1998). Utilization of Pine Kraft lignin in starch composites: Impact of structural heterogeneity. *Journal of Agricultural and Food Chemistry*, *46*, 2234–2240.

Baumberger, S., Lapierre, C., Monties, B., Lourdin, D., & Colonna, P. (1997). Preparation and properties of thermally molded and cast lignosulfonates–starch blends. *Industrial Crops and Products*, *6*, 253–258.

Baumberger, S., Monties, B., & Valle, G. D. (1998). Use of Kraft lignin as filler for starch films. *Polymer Degradation and Stability*, *59*, 273–277.

Beach, F. D., Boyd, R., & Uri, N. D. (1995). The effects of increasing biodegradable polymer resin use on the U.S. economy. *The Science of the Total Environment*, *175*, 219–233.

Carvalho, A. J. F., Curvelo, A. A. S., Zambon, M. D., & Gandini, A. (2003). Size exclusion chromatography characterization of thermoplastic starch composites 1. Influence of plasticizer and fibre content. *Polymer Degradation and Stability*, *79*, 133–138.

Chen, Y., Fringant, C., & Rinaudo, M. (1997). Molecular characterization of starch by SEC: Dependence of the performances on the amylopectin content. *Carbohydrate Polymers*, *33*, 73–78.

Coultate, T. P. (1996). *Food—the chemistry of its components. The Royal Society of Chemistry Paperbacks* (3rd ed.) chapter III, p.29–53.

Forssell, P. M., Mikkilä, J. M., Moates, G. K., & Parker, R. (1997). Phase and glass transition behavior of concentrated barley starch–glycerol–water mixtures, a model for thermoplastic starch. *Carbohydrate Polymers*, *34*, 275–282.

Jarowenko, W. (1977). Starch based adhesives. In: *Handbook of adhesives* (2nd ed., pp. 192–211). New York: Van Nostrand Reinhold.

Mercier, C. M. (1977). Effect of extrusion-cooking on potato starch using a twin screw French extruder. *Die Stärke*, *29*, 48–52.

Millard, M. M., Wolf, W. F., Dintzis, F. R., & Willet, J. L. (1999). The hydrodynamic characterization of waxy maize amylopectin in 90% dimethyl sulfoxide–water by analytical ultracentrifugation, dynamic, and static light scattering. *Carbohydrate Polymers*, *39*, 315–320.

Peng, W., Riedl, B., & Barry, A. O. (1993). Study on the kinetics for lignin methylolation. *Journal of Applied Polymer Science*, *48*, 1757–1763.

St-Pierre, N., Favis, B. D., Ramsay, B. A., Ramsay, J. A., & Verhoogt, H. (1997). Processing and characterization of thermoplastic starch/polyethylene blends. *Polymer*, *38*, 647–655.

Tudorachi, N., Rusu, M., Cascaval, C. N., Constantin, L., & Rugină, V. (2000). Biodegradable polymeric materials. 1. Polyethylene-natural polymer blends. *Cellulose Chemistry and Technology*, *34*, 101–111.

Whistler, R. L., Bemiller, J. N., & Paschall, E. F. (1984). *Starch: Chemistry and technology*. New York: Academic Press chapter VI.

Wiedmann, W., & Strobel, E. (1991). Compounding of thermoplastic starch with twin-screw extruders. *Starch-Starke*, *43*, 138–145.

Willet, J. L., Millard, M. M., & Jasberg, B. K. (1997). Extrusion of waxy maize starch: Melt rheology and molecular weight degradation of amylopectin. *Polymer*, *38*, 5983–5989.

Young, A. H. (1984). Fractionation of starch. In R. L. Whistler, J. N. Bemiller, & E. F. Paschall (Eds.), *Starch: Chemistry and technology*. 2nd ed. San Diego, CA: Academic Press chapter VIII.