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Rheological properties of thermoplastic starch and starch/poly(ethylene-*co*-vinyl alcohol) blends*

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Blends consisting of a systematic compositional series of starch/poly(ethylene-*co*-vinyl alcohol) were studied by using capillary viscometry. Three different types of starches were used: waxy maize, a starch containing essentially 100% amylopectin; native corn, possessing approximately 70% amylopectin and 30% amylose; and a treated, high-amylose starch, consisting of approximately 30% amylopectin and 70% amylose. Poly(ethylene-*co*-vinyl alcohol) with 44 mol% ethylene was blended in varying proportions with the starches, and glycerine and water were added as plasticizers.

The viscosity of the blends was measured over the shear-rate range 1–1000 s^{-1}. Samples unconditioned (as stored) as well as conditioned at 65% relative humidity and 23°C were measured at temperatures between 140 and 170°C. All viscosity results fall in the power-law regime, and there is no indication of approach to a zero-shear-rate viscosity in any of the starch blend systems.

As in starch-based food materials, the viscosity has an Arrhenius dependence on temperature, an exponential dependence on moisture content and a power-law dependence on shear rate. The power-law exponents from the starch blends are less than unity, indicating that the melts are shear thinning. Results on the starch/poly(ethylene-*co*-vinyl alcohol) blends indicate that the viscosity decreases with decreasing amylose content or increasing poly(ethylene-*co*-vinyl alcohol) content. The shear-rate dependence increases with an increase in the amylose content of the blends.

(Keywords: biodegradable blends; starch/EVOH; rheology)

INTRODUCTION

Increasing environmental concerns have renewed interest in the development of biodegradable materials. Among these materials, biodegradable plastics will be important in applications for articles that are unlikely to be recycled, such as trash/rubbish and compost bags, mulch films and disposable diapers/nappies. Considerable interest has been shown for the potential use of starch-based polymer blends to produce biodegradable plastics for such applications. For example, films of starch/poly(ethylene-*co*-acrylic acid) plasticized by urea have been studied in order to improve starch-based films designed for biodegradable agricultural mulch[1–6].

In order to replace more readily common thermoplastics in commodity applications, starch blends must be processable in existing, standard equipment, and must provide comparable mechanical properties and stability to the non-degradable thermoplastics they replace. This straightforward substitution of polymer in existing processes is difficult because, although starch can be thermoplastically processed under special conditions (i.e. limited ranges of pressure, temperature and moisture), starch itself cannot be considered as a typical thermoplastic polymer.

Starch, a major structure-forming food hydrocolloid, is a polymeric mixture of essentially linear (amylose) and branched (amylopectin) α-D-glucan molecules. Small amounts of non-carbohydrate constituents (lipids, phosphorus and proteins) present in native starch also contribute to its functionality[7]. Starch is found in a granular form, in which amylopectin and possibly amylose molecules are radially arranged towards the granular surface. Maize starch granules range from 10 to 25 μm in diameter and are mostly polyhedral in shape[7]. For most starches, crystallinity is attributed to short degree of polymerization (*DP*) chains of amylopectin (14–20 glucose units)[8]. The amorphous phase of granular starch is also heterogeneous, consisting of amorphous amylose and intercrystalline regions of dense branching in amylopectin. The implication of such complex morphology is that the thermal properties and plasticization behaviour of starch by water will vary throughout the amorphous phase[9].

During extrusion, shearing forces tear apart the starch granules and allow faster transfer of water into the interior. Under extrusion at low moisture content, a mixture of small amounts of gelatinized and melted starch

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as well as fragments of starch granules exist in the extruder simultaneously[10]. The mechanism of fragmentation is reported to be in the form of limited debranching of amylopectin, which causes a significant decrease in overall molecular weight. Fragmentation is also thought to be in the form of random chain scission in amylose[11]. Fragmentation of starch during extrusion depends on the operating conditions of the extruder (screw speed, temperature and moisture content) as well as the type of starch used[12,13].

The rheological behaviour of cereal doughs (containing over 50% water and at low temperature) has been studied by using capillary rheometry or viscometer dies attached to extruders[14]. However, the behaviour during extrusion of low-moisture-content starch is completely different: the classical phenomenon of gelatinization at 60–80°C cannot be involved because in the extruder the amount of water is limited (less than 50%). Under extrusion conditions, the transformation of starch occurs by melting of the crystallites, leading to a molten phase, the existence of which was demonstrated by investigations with an extruder whose barrel could be opened[15].

Senoucci and Smith have shown that the effect of mechanical degradation is more important at low temperatures, whereas at high temperature, thermal degradation dominates. On the other hand, higher temperatures also result in a more Newtonian response at constant screw speed[16].

Depending on the severity of thermomechanical conditions (temperature, pressure and shear history of the starch), moisture content and presence of other constituents, separation of amylose and amylopectin phases can take place during processing, thereby resulting in a composite structure of the product. The complex interplay between these structural components and the effect of solvent (plasticizer) on the physicochemical properties and stability of processed starch matrices is not yet fully understood. Also of great interest are the processing conditions under which the various types of supramolecular structure in the finished product are obtained[13].

Vergnes *et al.*[17] studied the rheological behaviour of molten corn starch with a 'pre-shearing rheometer', which allows well characterized thermomechanical treatment of the sample immediately preceding viscosity measurements. The 'pre-shearing rheometer' has the combined features of a Couette rotational system, which allows mechanical treatment consisting of a known shear strain and residence time to be applied, and a capillary viscometer, by which viscosity can be measured. The shear rate, melt temperature and time of shearing could be closely controlled independently. Viscosity measurements were made on commercial corn starch; and the influence of temperature, moisture content and intensity of the pre-shearing were studied. The results show that the dependence of viscosity on the shear rate can be described by a power law, in which the power-law parameters depend on temperature, moisture content and thermomechanical treatment. Their results indicate that viscosity decreases when temperature and water content increase for a fixed thermomechanical treatment. Viscosity decreases with increasing intensity of treatment, and the effect is more pronounced at higher temperatures. A direct correlation between the degree of macromolecular degradation, measured by intrinsic viscosity or water solubility, and the degree of thermomechanical treatment was also found.

Lai and Kokini[18] studied the effects of extrusion processing variables (such as melt temperature, screw speed and moisture content), amylopectin/amylose ratio and extent of starch conversion on the apparent viscosity of starch dough through the application of a capillary die and a slit die viscometer attached to a single-screw extruder. The term 'conversion' was used instead of gelatinization because, during extrusion–cooking at low moisture content, a mixture of gelatinized and melted states of starch as well as intermediate states exists. Their results also suggest that increasing melt temperature or moisture content reduce the viscosity. Both shear force and thermal energy contribute to starch conversion. Higher temperature and lower moisture content gave rise to a higher extent of starch conversion. A 70% amylose starch (Hylon VII) gave a higher overall viscosity and was gelatinized less than 98% amylopectin starch (Amioca); this was attributed to the structural difference between these two corn starches.

Starch is hydrophilic and its moisture content depends on the relative humidity of the atmosphere in which it is stored. The glass transition temperature of native starch is a strong function of the moisture content. Because of the hygroscopic nature of starch and its poor mechanical properties, and the sensitivity of these properties to water content in the solid polymer product, it is necessary to blend thermoplastic starch with other synthetic polymers[19] for many practical applications. Poly(ethylene-*co*-vinyl alcohol) (EVOH) is a good candidate as the synthetic polymer in the blends, because the hydroxyl groups promote compatibility with starch and ethylene groups can provide hydrophobicity or at least ameliorate the problems associated with the hygroscopic character of starch.

Although there have been valuable contributions relating to rheological properties of pure starch, for biodegradable thermoplastic blends there is still a need to understand how the processing conditions, synthetic polymer, as well as type and amount of plasticizers can affect processability and mechanical and rheological properties of the blends[20]. Therefore, in this work a series of blends of starches with different amylose and EVOH contents were studied. This paper reports on the systematic characterization of the melt viscosity of thermoplastic starch and starch/EVOH blends.

EXPERIMENTAL

Materials

Three different types of starches were used: waxy maize (Amioca), a starch containing essentially 100% amylopectin; native corn (Melojel), possessing approximately 70% amylopectin and 30% amylose; and a treated, high-amylose starch (Hylon VII), consisting of approximately 30% amylopectin and 70% amylose. A synthetic polymer, poly(ethylene-*co*-vinyl alcohol) with 44 mol% ethylene (EVAL E105), number-average molecular weight approximately 50 000 and polydispersity index (M_w/M_n) around 2.0, was utilized. Poly(ethylene-*co*-vinyl alcohol) was blended in varying proportions with the starches. Glycerine was added as a plasticizer in the amount of approximately 15% of the total weight of these blends. Water was also added during compounding. Finally, naturally occurring emulsifiers, such as glycerides, lipids and fatty acids, were added in small amounts (< 1%) (see *Table 1*).

The blends were prepared at Novon (Warner–Lambert, Morris Plains, NJ) with a 34 mm co-rotating Leistritz twin-screw extruder. Dry feed, consiting of starch powder, EVOH pellets and glycerides, was previously dry blended. Glycerine and water were pumped through a liquid port. After passing from the extruder, the blends were cut into pellets and cooled by air flow on a spiral conveyer. Pellets were collected and sealed in plastic bags. *Table 1* lists the series of blends used in this work, the compounding parameters[21] and the total output flow rate obtained from a mass balance in the system. The total output flow rate was approximately 11 to 14 kg h^{-1} for the neat starches and around 20 kg h^{-1} for the blends. Feed rates and the resulting blend compositions inside the extruder are shown in *Table 2*. Inside the extruder, the amount of plasticizers (water and glycerine) varied from 22.6 to 35 wt%. The average weight per cent of plasticizers was around 25, 30 and 33 wt% in blends containing waxy maize, native corn and high-amylose starch, respectively. All blends were run at 110 to 160 r.p.m., and the peak temperature was 190°C except for NC-100 and HY-100, where the temperature had to be lowered.

Table 1 Blend compositions and compounding parameters for starch/poly(ethylene-*co*-vinyl alcohol) blend series

Nomenclature	Starch (wt%)[a]	R.p.m.	Extruder peak temperature (°C)	Output flow rate (kg h^{-1})[b]
Waxy maize				
WM-100	100	131	190	11.4
WM-70	70	114	190	17.3
WM-50	50	115	190	19.2
WM-30	30	129	190	17.7
Native corn				
NC-100	100	160	119	14.2
NC-70	70	120	194	19.8
NC-50	50	125	190	19.2
NC-30	30	137	190	18.3
Hylon VII				
HY-100	100	150	170	13.4
HY-70	70	130	190	18.0
HY-50	50	149	190	19.8
HY-30	30	125	190	18.7

[a] Based on dry materials (starch and EVOH)
[b] Calculated from a mass balance

Table 2 Feed rates and blend composition inside the extruder during compounding

	Feed rate (kg h^{-1})			Blend composition (wt fraction)		
Blend	Solid[a]	Glycerine	Water	Solid[b]	Glycerine	Water
WM-100	9.8	1.7	0.0	0.750	0.150	0.100
WM-70	14.9	2.6	0.0	0.773	0.150	0.076
WM-50	15.7	2.8	1.5	0.732	0.138	0.130
WM-30	14.9	2.6	2.0	0.727	0.135	0.138
NC-100	11.6	2.0	1.5	0.671	0.134	0.195
NC-70	15.1	2.7	1.9	0.698	0.136	0.166
NC-50	15.3	2.7	2.1	0.706	0.133	0.161
NC-30	15.3	2.7	1.8	0.735	0.136	0.129
HY-100	11.6	2.0	1.2	0.686	0.137	0.177
HY-70	14.8	2.6	3.0	0.659	0.129	0.212
HY-50	15.4	2.8	3.8	0.651	0.126	0.224
HY-30	15.3	2.7	2.7	0.702	0.129	0.169

[a] Starch and EVOH conditioned at 50% r.h. at room temperature
[b] Starch or starch and EVOH

Table 3 Glycerine content and water content (weight per cent wet basis) in blends as compounded, as stored and conditioned at 65% r.h. at 23°C

	Glycerine content (wt%),	Water content (wt%)		
Blend	as stored[22]	As compdd[22]	As stored	Conditioned
WM-100	16.1	7.8	6.0	9.5
WM-70	16.3	5.3	4.0	8.3
WM-50	14.8	9.0	6.7	7.1
WM-30	12.7	7.5	5.6	6.0
NC-100	12.2	15.8	12.8	9.8
NC-70	18.1	12.7	9.9	8.5
NC-50	16.1	9.9	8.4	6.9
NC-30	13.6	6.8	5.0	5.9
HY-100	15.1	8.7	7.6	8.1
HY-70	14.8	10.6	10.0	7.9
HY-50	15.6	12.1	11.0	7.5
HY-30	14.1	8.0	5.8	5.9

Methods

In order to have controlled moisture content in the blends, it was necessary after compounding to condition the pellets to known moisture levels. This was accomplished by placing the pellets in a closed chamber at room temperature (23°C) and at 65% relative humidity (provided by a solution of glycerine and water) for at least one week before viscosity measurements were made. The water content of the pellets was measured by Karl Fisher titration with the Mettler DL 18 titration apparatus equipped with the DO-301 drying oven ($T = 200$°C, stir time = 20 min)[22]. The final glycerine content in the pellets was measured by h.p.l.c. in order to confirm that the desired glycerine levels were achieved[23].

Glycerine and water contents for the blends after compounding, as stored and after conditioning at 65% r.h. at 23°C are presented in *Table 3*. Samples after compounding and as stored present different moisture contents depending on the amount of water used during compounding. However, samples conditioned at 65% r.h. have almost the same moisture content for blends possessing approximately the same starch weight per cent. The equilibrium moisture content in the blends depends on the blend composition, varying from approximately 10% for the neat starch to 6% for the blends containing 30% starch.

The capillary viscometer used to determine the viscosity of the blends was an Instron model 3210 rheometer coupled with a model 4505 series universal testing instrument. The capillary viscometer consists of a barrel (with internal diameter of 0.952 cm and length of 28.8 cm) into which material was loaded before being pushed by a plunger through a capillary placed inside the barrel at the lower end. The temperature of the barrel and capillary was controlled by a surrounding heating unit. Shear stress and shear rate are obtained by measuring the force required to maintain a steady flow of material through a capillary for different, controlled plunger velocities. The results reported here were obtained by using a capillary with an inside diameter D of 0.0762 cm and a length L of 5.08 cm, giving an L/D of 66.7. Another two capillaries with approximately the same diameter and L/D values of 34.5 and 103.4 were also used to check for end effects in the capillary.

The material was poured into the barrel through a funnel and then packed down with the plunger until the first extrudate appeared at the capillary exit. The sample was allowed to come to temperature (5–10 min), and was then forced through the capillary by the plunger at pre-selected velocities. The next velocity in the measurement schedule begins when the load *versus* extension curve reaches a slope close to zero. The load on the plunger and the plunger speed provide the total pressure drop through the barrel and capillary and the volume flow rate Q. These are converted to the wall shear stress τ_R and the wall shear rate $\dot{\gamma}_R$ in the capillary by standard methods[24].

First the pressure gradient $\Delta p/L$in the fully developed shear flow region of the capillary is determined by subtracting off the pressure drops associated with the barrel and entrance and exit to the capillary test section. Entrance and exit effects in the capillary become important at small L/D ratios, and a Bagley correction for these 'elastic' end effects should be made by using capillaries of different lengths but with the same diameter. The Bagley correction results for the three L/D capillaries we used indicated that the end effects were negligible for the blends we studied. Finally, the wall shear stress in the capillary is:

$$\tau_R = \frac{\Delta p R}{2L} \tag{1}$$

Next the wall shear rate $\dot{\gamma}_R$ is calculated by differentiating the volume flow-rate data with respect to the wall shear stress:

$$\dot{\gamma}_R = \frac{1}{\tau_R^2} \frac{\mathrm{d}}{\mathrm{d}\tau_R}\left(\tau_R^3 \frac{Q}{\pi R^3}\right) \tag{2}$$

Equation (2) is known as the Weissenberg–Rabinowitsch equation. Once τ_R and $\dot{\gamma}_R$ are known, the viscosity is found from:

$$\eta(\dot{\gamma}_R) = \frac{\tau_R}{\dot{\gamma}_R} = \frac{\tau_R}{(Q/\pi R^3)}\left(3 + \frac{\mathrm{d}\ln(Q/\pi R^3)}{\mathrm{d}\ln \tau_R}\right)^{-1} \tag{3}$$

All viscosity data reported in this paper are true viscosity, equation (3), evaluated at the truc wall shear rate, equation (2). We were able to obtain shear rates in the range 1 to 1000 s^{-1} in our experiments.

Blends as stored as well as conditioned at known relative humidity (65% at 23°C) were measured at temperatures between 140 and 170°C. The lower temperature was set by the melting point of EVOH in the blends and the upper bound on temperature was determined by the onset of starch thermal degradation between two consecutive measurements.

RESULTS AND DISCUSSION

The dependence of food dough viscosity on temperature, moisture content and shear rate has been observed by a number of researchers[14,16,25–27]. In all these studies, the viscosity η of cereal dough has been found to have a power-law dependence on shear rate $\dot{\gamma}$, an Arrhenius dependence on temperature T, and an exponential dependence on moisture content MC (usually expressed as weight per cent wet basis):

$$\eta = m\dot{\gamma}^{n-1}\exp(\Delta H/RT)\exp(-kMC) \tag{4}$$

where m is the consistency index, n is the power-law exponent, ΔH is the flow activation energy, and k is the moisture dependence constant. Since for the shear-rate range attainable in this study all the testing occurred in the power-law regime, the same equation used to describe the viscosity of food doughs will be applied for the starch-based blends. We next describe the effects of starch type, concentration of synthetic polymer, concentration of water and temperature on the viscosity of molten blends.

Effect of starch type

Figure 1 shows viscosity results measured at 150°C for neat starches conditioned at 65% r.h. (approximate equilibrium moisture content 10%). Although the processing conditions for the three starch types were different, as shown in *Tables 1* and *2*, it is seen in *Figure 1* that waxy maize has a lower viscosity and higher power-law exponent (closer to unity) than native corn and high-amylose starch. Therefore, the results suggest that, as the amylose content in the starch is increased, the viscosity increases. Hylon VII exhibits the highest viscosity and the lowest power-law exponent. To understand this result, we note that amylopectin is a compact, highly branched molecule, whereas amylose is almost linear (it has a few long chain branches) and more flexible. A linear molecule generally will have a higher viscosity than a highly branched one, because it can become more entangled[28].

Viscosity results for blends containing 70% (dry basis) starch conditioned at 65% r.h. and measured at 150°C are shown in *Figure 2*. The results in this case validate the influence of amylose on the viscosity of the material.

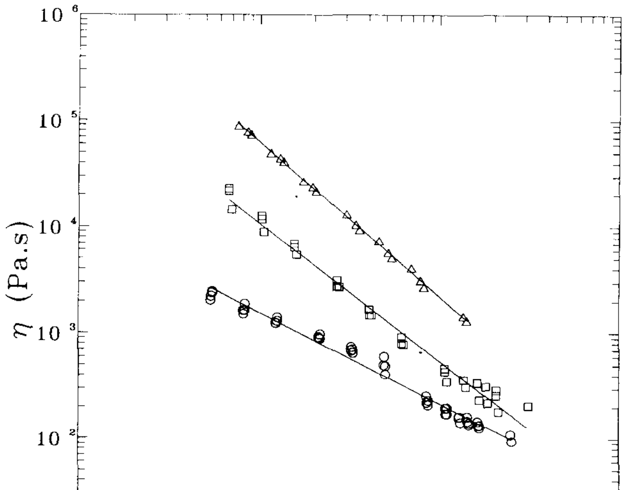

Figure 1 Influence of starch type on viscosity of blends containing 100 wt% starch (dry basis) conditioned at 65% r.h. at 23°C. Data are taken at T= 150°C: (○) waxy maize, (□) native corn, and (△) Hylon VII

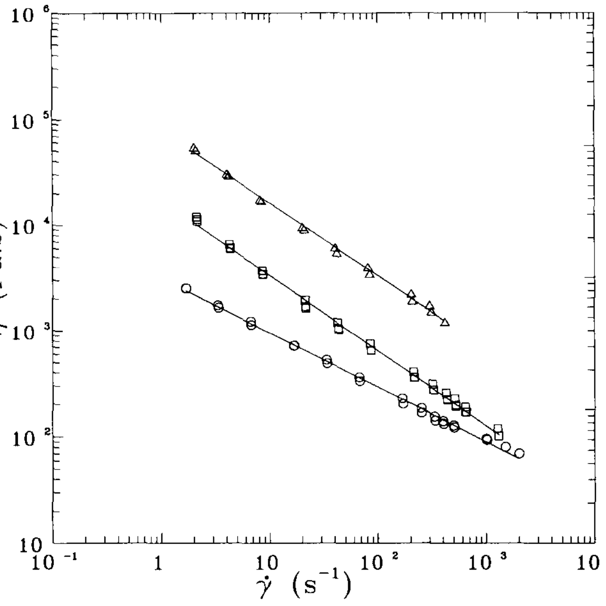

Figure 2 Influence of starch type on viscosity of blends containing 70 wt% starch (dry basis) conditioned at 65% r.h. at 23°C. Data are taken at $T = 150$°C: (○) waxy maize, (□) native corn, and (△) Hylon VII

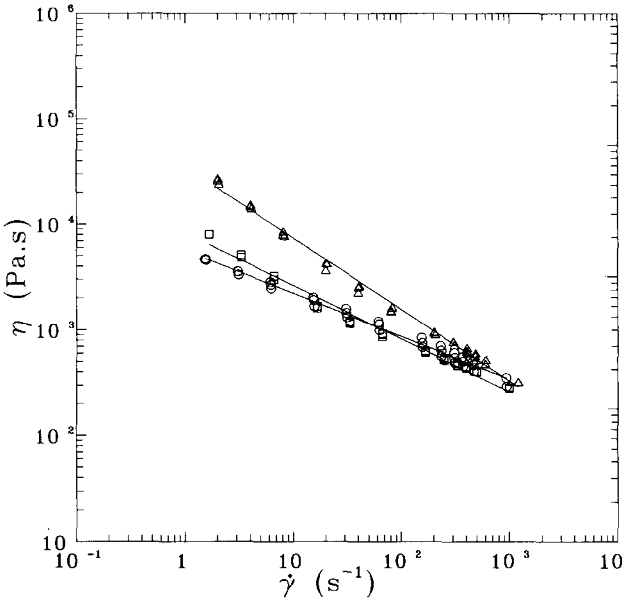

Figure 3 Influence of starch type on viscosity of blends containing 50 wt% starch (dry basis) conditioned at 65% r.h. at 23°C. Data are taken at $T = 150$°C: (○) waxy maize, (□) native corn, and (△) Hylon VII

The blend containing Hylon VII exhibits the highest viscosity, and the blend with essentially pure amylopectin shows the lowest viscosity. For these blends the processing conditions were similar (peak temperature and r.p.m.); the only significant processing difference was the lower plasticizer content in the waxy maize blend.

Figures 3 and *4* show the results for blends containing 50 and 30% starch, respectively, also conditioned at 65% r.h. and measured at 150°C. For blends with an EVOH content of 50% or higher, the synthetic polymer starts to dominate the viscous behaviour of the blends. Blends containing Hylon VII show higher viscosities than the blends compounded with native corn or waxy maize. Power-law exponents for these blends are higher than the corresponding values for blends with higher starch content. This indicates that the presence of the synthetic polymer leads to more Newtonian-like behaviour of the viscosity. *Table 4* summarizes the values of the consistency index *m* and the power-law exponent *n* for all the blends at 150°C.

Effect of EVOH content

The effect of synthetic polymer weight fraction on the viscosity is shown in *Figures 5–7*. For comparison, in each figure the viscosity of a blend of pure EVOH with 15 wt% glycerine also conditioned at 65% r.h. is shown. *Figure 5* shows the viscosity of blends containing waxy maize. For this polymer, the blends containing 50 and 30% starch exhibit higher viscosities than those for the 100 and 70% starch blends. A possible explanation for this behaviour is the influence that EVOH makes on the degradation of starch during the extrusion process. As the concentration of EVOH is increased, starch molecules

Table 4 Consistency index *m* and power-law exponent *n* for blends at 150°C as stored and conditioned at 65% r.h. at 23°C

	As stored		Conditioned	
Blend	*m* (Pa s^n)	*n*	*m* (Pa s^n)	*n*
WM-100	5950	0.458	3420	0.486
WM-70	5610	0.466	3130	0.485
WM-50	3700	0.543	5600	0.595
WM-30	3500	0.643	4770	0.633
NC-100	19 050	0.261	35 100	0.226
NC-70	14 000	0.286	17 200	0.288
NC-50	9230	0.429	8280	0.498
NC-30	5400	0.601	5150	0.613
HY-100	171 000	0.119	238 000	0.130
HY-70	24 700	0.269	79 300	0.240
HY-50	15 850	0.311	35 000	0.324
HY-30	7480	0.513	10 900	0.505

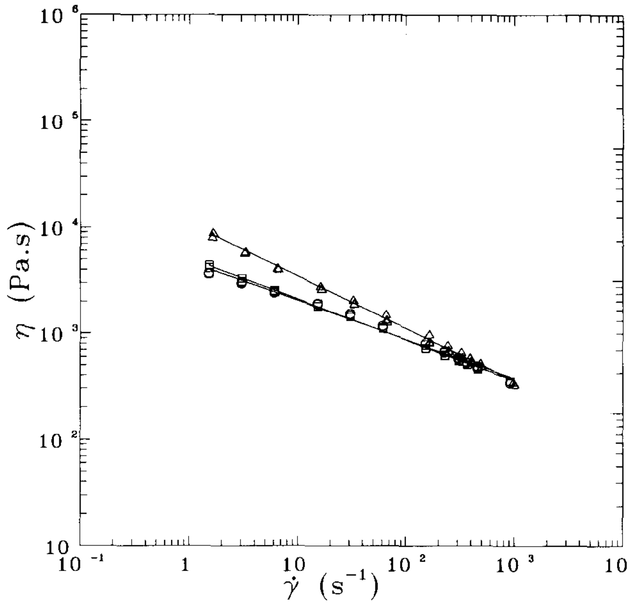

Figure 4 Influence of starch type on viscosity of blends containing 30 wt% starch (dry basis) conditioned at 65% r.h. at 23°C. Data are taken at $T = 150$°C: (○) waxy maize, (□) native corn, and (△) Hylon VII

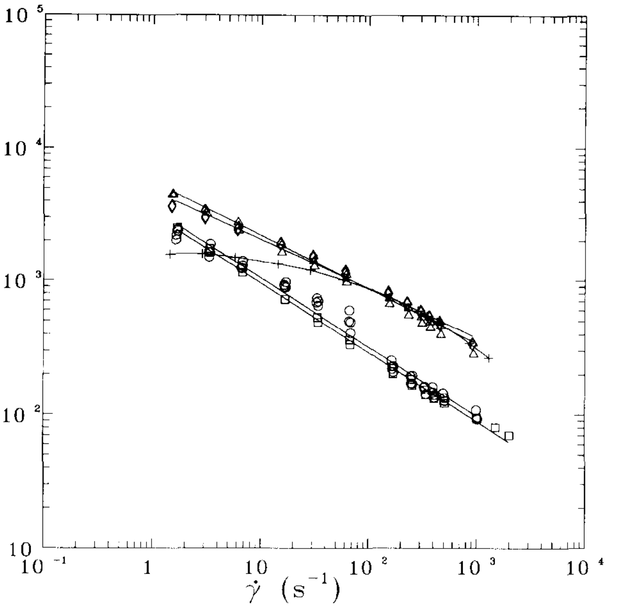

Figure 5 Influence of poly(ethylene-*co*-vinyl alcohol) content type on viscosity for blends containing waxy maize conditioned at 65% r.h. at 23°C. Data are taken at $T=150°C$: (○) WM-100, (□) WM-70, (△) WM-50, (◇) WM-30, and (+) WM-0

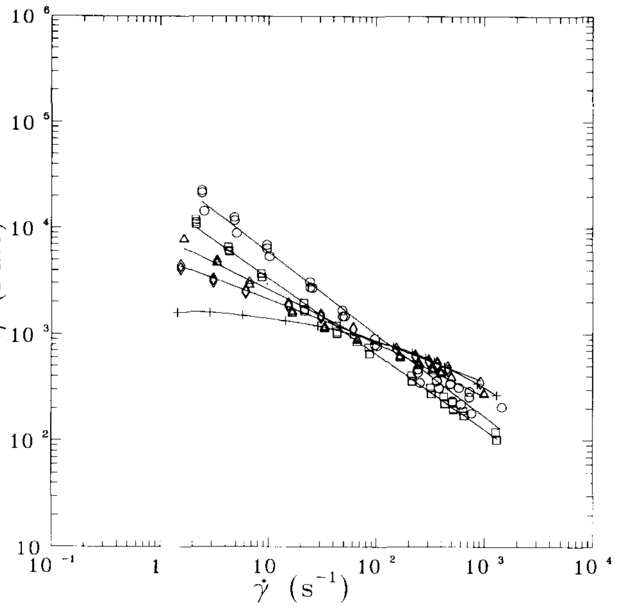

Figure 6 Influence of poly(ethylene-*co*-vinyl alcohol) content type on viscosity for blends containing native corn conditioned at 65% r.h. at 23°C. Data are taken at $T=150°C$: (○) NC-100, (□) NC-70, (△) NC-50, (◇) NC-30, and (+) NC-0

experience lower stress and therefore undergo less chain scission during compounding.

Blends containing native corn (*Figure 6*) show different behaviour. For blends containing 100 and 70% starch, the viscosity curves are almost parallel (approximately the same power-law exponent). The viscosity at lower shear rates decreases when the EVOH content is increased but the opposite behaviour is observed for high shear rates. In this regime the blends with higher EVOH content exhibit viscosity values closer to those of the neat EVOH than to those of the pure native corn.

The viscosity for higher-amylose-content starch blends is shown in *Figure 7*. The results indicate the same trend observed for native corn starch blends at low shear rates. At high shear rates, blends with higher starch content have, in this case, higher viscosities. Only the blends containing 50 and 70% EVOH yield viscosity values similar to the neat EVOH blends in the high-shear-rate regime.

Consistency index values presented in *Table 4* indicate that for blends containing amylose the viscosity at lower shear rates increases when the starch content in the blend increases. The *m* values for the waxy maize blends are relatively low, with the maximum value occurring for the 50% blend.

Power-law exponents increase when the EVOH content is increased. This result indicates that the blends with high EVOH content are more 'Newtonian', or less shear-rate-dependent (*Table 4*). The neat EVOH material approaches the zero-shear-rate viscosity at low shear rates, which explains the smaller degree of shear thinning for blends containing more than 50% EVOH.

Effect of water content

All blends were measured as stored as well as after being conditioned at 65% r.h. at 150°C in order to analyse the influence of water content. As expected, the viscosity decreases when the weight fraction of water is increased. *Figure 8* shows the viscosity of the blends containing 70% starch. For the conditioned blends, the moisture content was approximately 8.3%, whereas for the 'as-stored' materials, the moisture content was a function of the amount of water used during compounding. The power-law exponent is nearly independent of moisture contents in the range studied for a given starch source. However, the consistency index is sensitive to the plasticizer level in the blend. Power-law parameters are listed in *Table 4* for all the blends at 150°C.

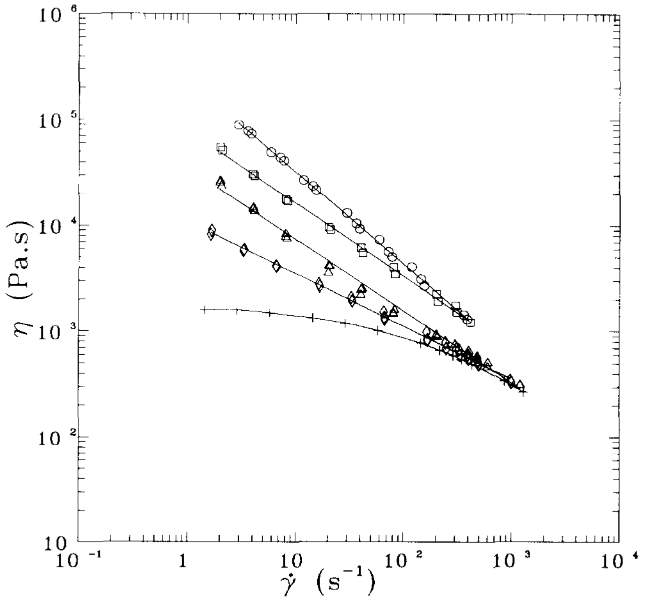

Figure 7 Influence of poly(ethylene-*co*-vinyl alcohol) content type on viscosity for blends containing Hylon VII conditioned at 65% r.h. at 23°C. Data are taken at $T=150°C$: (○) HY-100, (□) HY-70, (△) HY-50, (◇) HY-30, and (+) HY-0

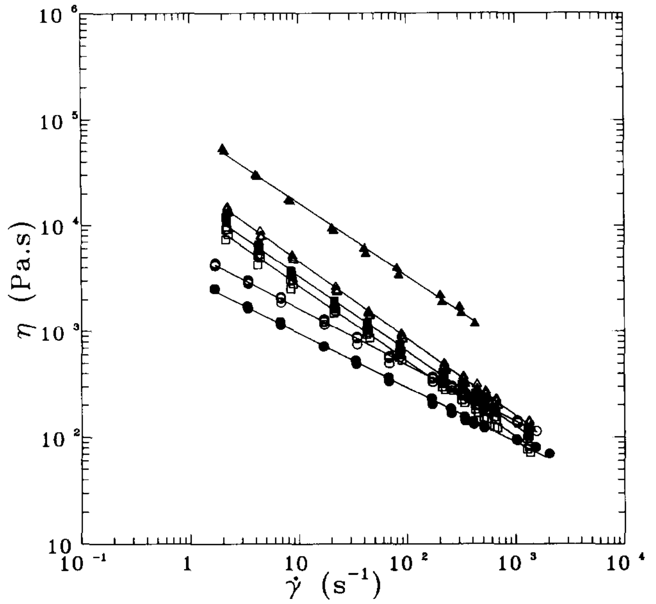

Figure 8 Influence of moisture content on corrected viscosity for blends containing 70 wt% starch (dry basis), 'as stored' (open symbols) and conditioned at 65% r.h. at 23°C (full symbols). Data are taken at T=150°C: (○) WM-70 (MC=4.0%); (●) WM-70 (MC=8.3%); (□) NC-70 (MC=9.9%); (■) NC-70 (MC=8.5%); (△) HY-70 (MC=10.0%); and (▲) HY-70 (MC=7.9%)

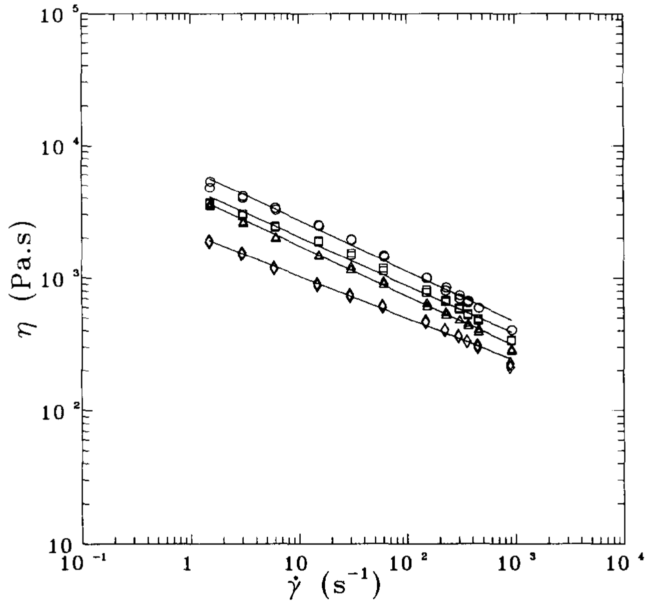

Figure 9 Influence of temperature on viscosity of blends containing 30 wt% waxy maize (dry basis) conditioned at 65% r.h. at 23°C: (○) T=140°C, (□) T=150°C, (△) T=160°C, and (◇) T=170°C

Effect of temperature

The temperature dependence of the viscosity is shown in *Figures 9–11* for blends containing 30% starch and conditioned at 65% r.h. The viscosity (at fixed shear rate and composition) of all materials tested was found to vary with temperature according to an Arrhenius expression. The flow activation energy, $\Delta H/R$, was calculated for each blend, and it is shown in *Table 5*.

For neat starches, the flow activation energy of waxy maize is three times higher than that of the native corn and Hylon VII, indicating that the rheological properties of the highly branched amylopectin are

Table 5 Flow activation energy for blends conditioned at 65% r.h. and 23°C

Blend	$\Delta H/R$ (K)
WM-100	11 700
WM-70	11 500
WM-50	10 900
WM-30	6820
NC-100	4360
NC-70	5660
NC-50	8650
NC-30	10 400
HY-100	4250
HY-70	3770
HY-50	4530
HY-30	4660

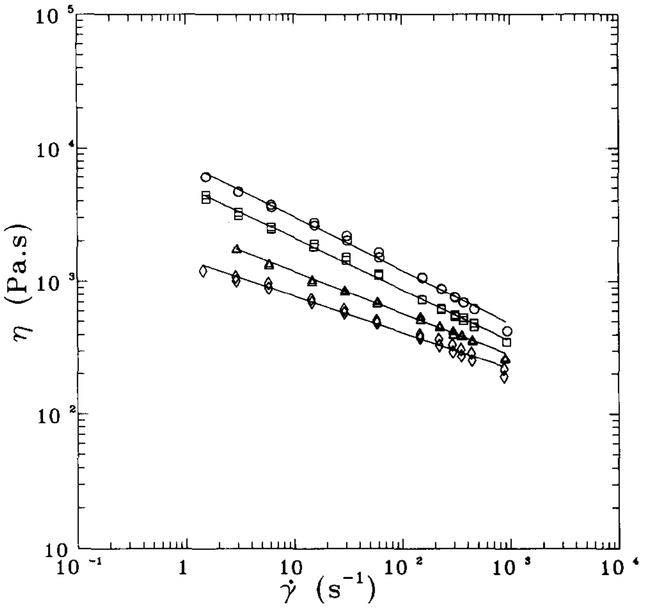

Figure 10 Influence of temperature on viscosity of blends containing 30 wt% native corn (dry basis) conditioned at 65% r.h. at 23°C: (○) T=140°C, (□) T=150°C, (△) T=160°C, and (◇) T=170°C

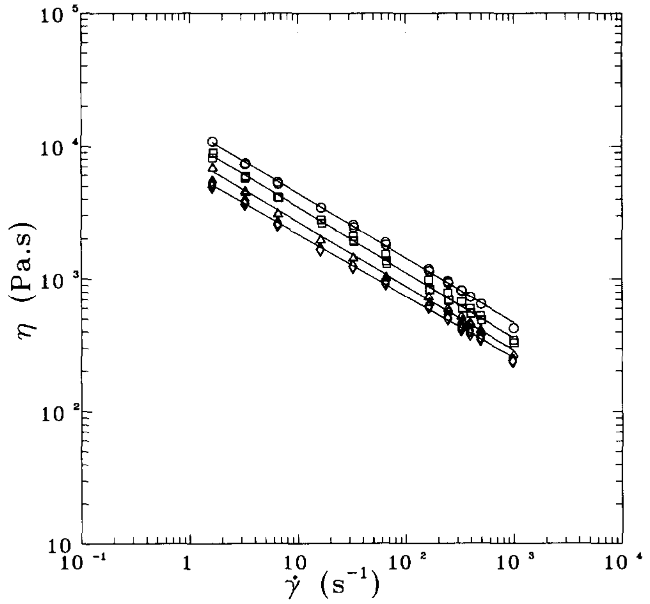

Figure 11 Influence of temperature on viscosity of blends containing 30 wt% Hylon VII (dry basis) conditioned at 65% r.h. at 23°C: (○) T=140°C, (□) T=150°C, (△) T=160°C, and (◇) T=170°C

more temperature-sensitive than those of the amylose component. When the EVOH content increases, the flow activation energy decreases for waxy-maize-containing blends, it is almost constant for Hylon VII blends, and it increases significantly for native corn blends. The values of flow activation energy found for plasticized neat starches are in good agreement with previous results reported in the literature[17,18].

CONCLUSIONS

Thermoplastic starches and starch/poly(ethylene-*co*-vinyl alcohol) blends are shown to be pseudoplastic with power-law exponents varying from 0.11 to 0.72 in the temperature range between 140 and 170°C and moisture contents between 4 and 13 wt%. The viscosity of these materials, as in the case of food starch materials, exhibits an Arrhenius dependence on temperature, an exponential dependence on moisture content and a power-law dependence on shear rate.

Results obtained for starch and starch/EVOH blends show that decreasing amylose or increasing EVOH content reduces the viscosity of the blends. This fact is consistent with the picture that amylose is more entangled than amylopectin, which leads to a higher overall viscosity. The shear-rate dependence increases when the amylose content of the blends is increased.

The flow activation energy, $\Delta H/R$, which characterizes the temperature dependence, is a function of the EVOH content and starch type. Results show that rheological properties of waxy maize blends are more temperature-sensitive than those of starch containing amylose.

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