Rheological Properties of Starch-Based Materials and Starch/Poly(lactic acid) Blends

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Summary: The rheological properties of pure starch and blends of gelatinized starch/poly(lactic acid) (PLA) were studied using a rheometer incorporating a twin-roll mixer and a single-screw extruder. The mixer provides a useful and convenient tool to study the rheological properties and gelatinization processes of starch. The single-screw extruder with a slit capillary die was used to measure shear stress and viscosity under different shear rates at different temperatures. Starch was shown to increase the shear viscosity of PLA. Methylenediphenyl diisocyanate (MDI) was used as a compatibilizer, and was distributed in different phases through controlled processing. The addition of MDI showed a stronger effect on rheological properties when it was distributed in the PLA phase prior to blending. Both the pure starch and blends showed a power law dependence of viscosity on shear rate.

Keywords: blends; compatibilizer; polyesters; rheology; starch

Introduction

Starch-based materials have attracted an increasing amount of attention over the last two decades, predominantly due to two major factors: firstly environmental concerns, and secondly the realization that our petroleum resources are finite. A third very important for factor of this kind for many countries is the desire to add value to agriculture products. One of the unique characteristics of starch-based materials is their processing properties, which involve starch swelling, gelatinization, melting, crystallization, decomposition etc.[1–3] However, the moisture sensitivity of pure starch-based materials limits their general application. Blending cheap thermoplastic starch with water-resistant biodegradable aliphatic polyester has attracted significant interest in both the scientific and commercial domains, since it could lead to the development of a range of new biodegradable polymeric materials.[4–7] The processing properties of starch and aliphatic polyesters are significantly different, in particular their rheological behaviour. The viscosity of starch is much higher than that of conventional polymers, whilst the viscosity of biodegradable aliphatic polyesters is relatively low. In this work, the rheological properties of cornstarch and blends of gelatinized starch/poly(lactic acid) (PLA) were studied using a rheometer with a twin-roll mixer and a single-screw extruder.

Experimental Part

Cornstarch was used as a model material in this experimental work to study the rheological properties of pure starch. The rheological behaviour of the starch during heating was firstly evaluated using a HAAKE Torque Rheometer Rheomix 600p with a twin-roll mixer. The variation of torque with time and temperature was used to investigate the gelatinization processes and rheological behaviour of the starch. Various rotation speeds (15, 25, 35, 45 RPM) were used in the experimental

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work to evaluate the relationship between shear stress and gelatinization.

The semi-crystalline PLA (Grade 4051) used in the experimental work was a commercially available product from NatureWork. Starch/PLA blends were firstly compounded using a twin-screw extruder (Ø30, L/D 40), and the resultant palletized extrusions were used to study the rheological properties. A HAAKE Rheocord Polylab RC 500p plus a single-screw extruder (Rheomex 252p, Ø19, Screw 2:1, L/D 25) with a slit capillary die (20×1 mm) was used to measure shear stress and viscosity under different shear at different temperatures. The starch-based materials were also firstly compounded using the twin-screw extruder at a water content 30%. The extrusion speeds used for all materials were between 30 and 200 revolutions per minute (rpm), which are similar to those used in industrial extrusion processing, and 6 points were recorded using automatic measurement.

Results and Discussions

Figure 1 shows the variation in torque with increasing time and temperature at different rpm, as measured by the HAAKE Rheometer. The initial temperature was set at 30 °C. Temperature increased with time due to shear stress and heat release during starch gelatinization. As shown in the figure, two torque peaks were detected at different rpm, with the first peak corresponding to the addition of starch into the mixer. The second peak represents that maxim point for the viscosity caused by swelling of starch granules. After the initial starch loading peak, torque increased with increasing time and temperature, before reaching a second peak. As expected, the time to achieve this second peak depended on rpm and temperature. After this peak, as the starch gelatinized, torque decreased with increasing time and temperature, until reaching a constant as viscosity stabilized. As seen, higher RPM rates resulted in higher final temperature and lower torque. Table 1 lists the effect of RPM on the parameters measured during processing. It is seen that the torque of both second peak and finished (10 min) was increased with increasing RPM, while the time to achieve the send peak was decreased with increasing RPM. It is noted that the increase rate of the torque (both second peak and final) with RMP is not linear, which indicates the materials is not a Newtonic system. The following study through measuring the shear stress and viscosities shows similar results.

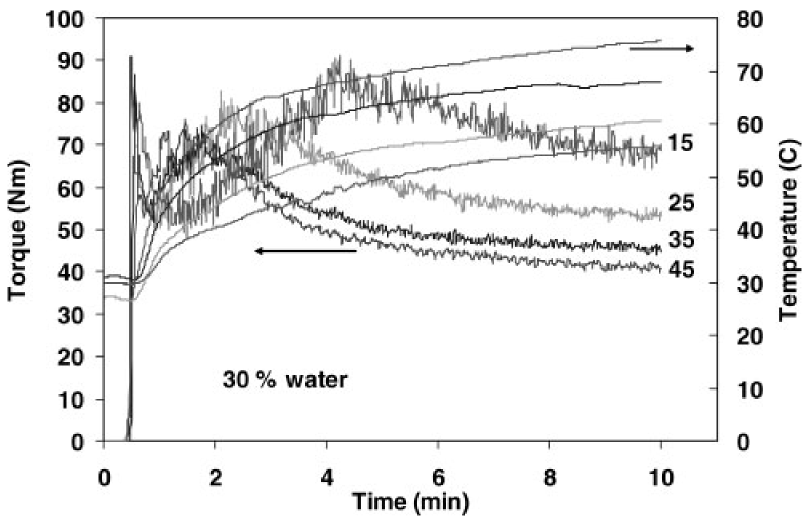

Figure 1.
Variation in torque with increasing time and temperature at different rpm for cornstarch.

Table 1.
Effect of RPM on the parameters measured by Rheomix.

Roller speed (RPM)	Torque of first peak (N.m)	Torque of second peak (N.m)	Time to second peak (min)	Finial torque (10 min) (N.m)	Finial Temp (10 min) (°C)
15	90	88	4.3	66	77.0
25	92	78	2.4	53	68.5
35	91	72	2.1	47	61.5
45	90	70	1.9	42	57.0

The simplest way to study starch gelatinization is to monitor processing under shearless conditions. The technologies developed include microscopic observation; differential scanning calorimetry and X-ray diffraction, FTIR and NMR et al. However, with the increasing use of starch in processes involving shear conditions, such as extrusion cooking and the production of thermoplastics, the study of gelatinization mechanisms under shear stress has both scientific and commercial importance. The techniques developed for food study are only suitable for studying starch gelatinization at low starch concentrations (about 0.5–20%). The HAAKE Torque Rheometer Rheomix provides a convenient tool to study the rheological properties and gelatinization processes of starch, in particular for the system with lower moisture content. Furthermore, since the twin rollers act as a screw element in a twin extruder, the results provide useful data for the screw design used for starch extrusion.

The samples collected from the mixer at different time and temperatures were studied by microscope and DSC to establish the relationship between torque detected and gelatinization measured. The results are corresponded with each other.

The shear stress and viscosities of the gelatinized cornstarch under different shear rates were measured using a HAAKE Rheocord incorporating a single-screw extruder with a slit capillary die at different temperatures. Starch and water were firstly premixed in a high speed mixer for 5 min then compounded using a twin-screw extruder (Ø30, L/D 40) with the highest barrier temperature 170 °C. The die temperature was set up at 110 °C and screw speed was 120 RPM during the compounding. Palletized materials were used to study their rheological properties.

Figure 2 shows the effect of temperature on the melt viscosity of cornstarch with 30% moisture content. It can be seen that viscosity was decreased with increasing

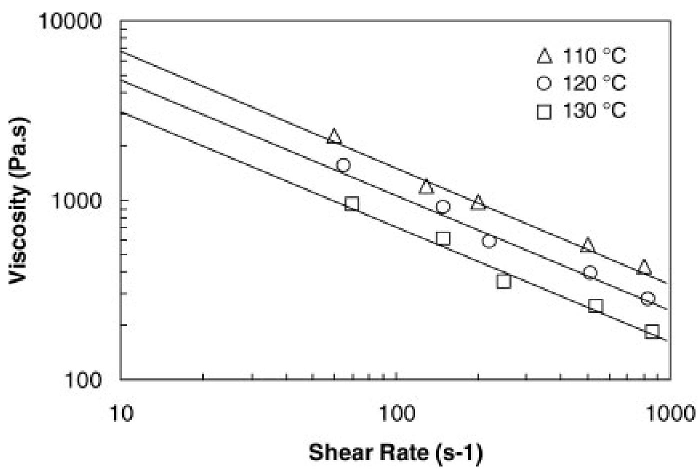

Figure 2.
Effect of temperature on melt viscosity of cornstarch.

shear rate at different temperature. It is noted that the dependence of viscosity on shear rate was linear on the double-logarithmic plot, indicating that the powder law model could represent the rheological behaviour of the molten materials, i.e.:

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

where η is shear viscosity and γ is shear rate.

Similar as other thermoplastic materials, the melt viscosity of cornstarch decreases with increasing temperature. This trend was observed regardless of moisture content during the pelletizing stage and viscosity measurements. It is important to point out the molecular weight of a starch is generally 100 times larger than conventional polymers and the molecular weight could be decreased significantly during extrusion. The compounding conditions will significantly affect the rheological properties. There is no means to compare the results with different compounding conditions.

Biodegradable polyesters have been used to improve the moisture sensitive of starch-based materials. Poly (lactic acid) (PLQA) was used as a model materials in this work. The shear stress and viscosities of the blends of starch/PLA under different shear rates were also measured by HAAKE Rheocord. Figure 3 shows the effect of temperature on the melt viscosity of PLA/starch blends. It can be seen that viscosity was decreased with increasing shear rate at different temperature. It is noted that the dependence of viscosity on the shear rate was linear on double-logarithmic plots, again indicating that the powder law model could represent the rheological behaviour of these molten materials. It can be seen that the melt viscosity of the blends increased with increasing starch content, however it should be noted that the increase rate was not linear. There was only a slight increase in viscosity when the starch content was lower than 30%, after which the difference can be more clearly identified. It is expected since the viscosity of starch is much higher than that of PLA. When the starch content is lower, it only acts as filler that slightly increased the viscosity. The starch phase gradually become a co-continuous then continues phase when the content is above 30%.

Figure 4 shows the effect of the compatibilizer methylenediphenyl diisocyanate (MDI) on the rheological properties of a PLA 70/starch 50 blend. The viscosities as a function of shear rate for the blends with MDI distributed in different phases were measured at 180 °C. It can be seen that the MDI did not affect the viscosity of the PLA/

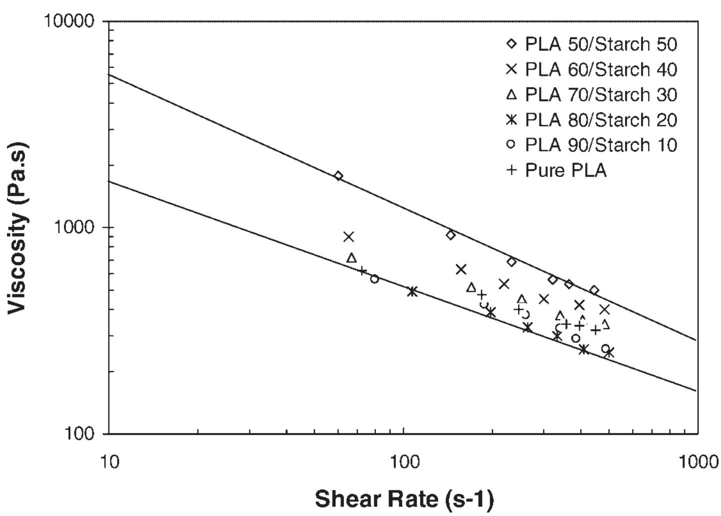

Figure 3.
Effect of starch content on the viscosity of PLA/starch blends.

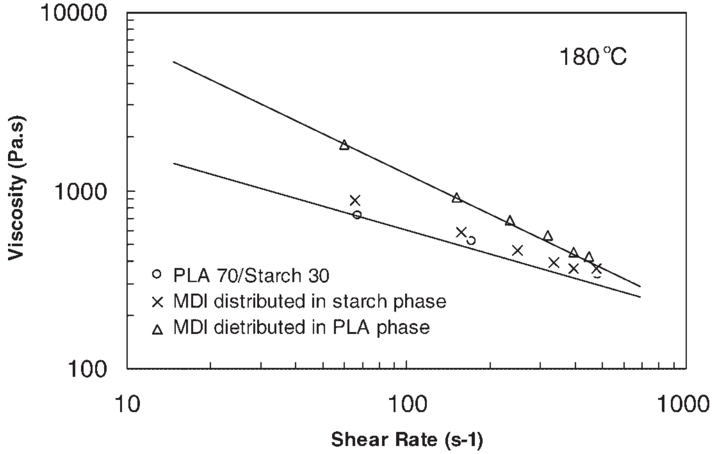

Figure 4.
Effect of MDI distribution on the melt viscosity of a PLA 70/starch 30 blend.

starch blend when it was distributed in the starch phase, while it increased viscosity when it was distributed in the PLA phase. Explanation for this is that the moisture containing in starch phase destroyed the function group in MDI. A strong power law dependence of viscosity on shear rate is also observed. For all the blends and measurement conditions in the experimental work, the dependence of viscosity on the shear rate was linear on double-logarithmic plots, indicating that the powder law model could represent the rheological behaviour of the molten blends. It should be noted that the effect of MDI on the rheological properties of a blend was not constant, i.e. the viscosity increased more in the lower shear rate range. Similar results were also observed for Bionolle/starch and PCL/starch blends.

Conclusions

The HAAKE Torque Rheometer Rheomix is a useful and convenient tool to study the rheological properties and gelatinization processes of starch. In this study, two torque peaks were detected for pure starch, which represent lording and maxim of viscosity. The higher rpm rates resulted in higher final temperature and lower torque. The dependence of viscosity of the starch on shear rate was linear on the double-logarithmic plot, indicating that the powder law model could represent the rheological behavior of the starch-based materials. Similar as other thermoplastic materials, the melt viscosity of cornstarch decreases with increasing temperature. This trend was observed regardless of moisture content during the pelletizing stage and viscosity measurements.

The shear stress and viscosities of gelatinized cornstarch and PLA/starch blends under different shear rates were measured using a HAAKE Rheocord incorporating a single-screw extruder with a slit capillary die at different temperatures. Both pure starch and blends showed a similar pattern of power law dependence of viscosity on shear rate. For all blends and measurement conditions, the dependence of viscosity on the shear rate was linear on double-logarithmic plots, indicating that the powder law model could represent the rheological behaviour of the molten starch and blends. The compatibilizer MDI did not affect the viscosity of the PLA/starch blends when it was distributed in the starch phase, while it increased viscosity when it was distributed in the PLA phase.

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