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Effects of glycerin and glycerol monostearate on performance of thermoplastic starch

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The effects of glycerin and glycerol monostearate (GMS) on a variety of properties of anhydrous wheat starch are explored by means of DSC, TGA, as well as mechanical, rheological and moisture sorption assessment. It is found that, as glycerin content (GC) increases, both melting point and degradation temperature decrease, and the range of the processing window extends. Melt viscosity of the glycerin-plasticized starch depends on shear rate following power law, exponentially on GC, and on temperature in Arrhenius type. Increasing GC leads to a linear increment of the equilibrium moisture sorption, which, however, can be depressed significantly by incorporating a small amount of GMS. Moreover, the presence of 2% GMS in the formulations can efficiently reduce the melt viscosity and enhance its temperature sensitivity while has insignificant effect on the non-Newtonian behaviour and mechanical properties.

1. Introduction

As a result of environmental concern, thermoplastic starch (TPS) has recently found itself in extensive applications as an alternative to petrochemical synthetic polymers. Great attentions have been put into exploring the extrusion processability of starch in powder-, dough- or grit-form [1–4]. The dependence of apparent viscosity on shear rate, processing temperature and moisture content has been modelled based on power law. The apparent viscosity of cereal starch during extrusion was shown to be pseudoplastic with power law index values from 0.25 to 0.75 in the temperature range between 67 °C and 158 °C and at a moisture content between 13% and 50%. The models have also been proved applicable for water-plasticized TPS [5]. It was reported that the TPS melt viscosity was more dependent on the moisture content than the processing temperature and shear rate. This effect primarily originated from water-catalysed hydrolysis at a high moisture level or the shear stress-induced chain scissions at a low moisture level due to the hygroscopic nature of starch. An optimum moisture content was therefore recommended to exist somewhere between 20% and 30%.

Glycerin destructurized TPS in presence of water has recently been investigated in terms of glass transition behaviour, crystallinity, plasticisation behaviour, mechanical and rheological properties [6–14]. In principle, a continuous decrease in glass transition temperature T_g occurs as the glycerin content (GC) increases. This has been modelled successfully. Because of the strong interaction between glycerin and starch, the presence of glycerin leads to a beta relaxation for the slightly hydrated starch, as well as a depression of retrogradation of waxy maize starch in presence of water. A significant change in crystallinity induced by the presence of glycerin, as well as the typical plasticizer diluting effect can contribute to great variations of mechanical properties of TPS.

Effects of a variety of additives have been investigated on rheological behaviour of TPS. Potente [15] reported that the melt viscosity of water-plasticized TPS increased with ammonium hydroxide, and reduced with urea and propylene glycol while unchanged with triethylene glycol (TEG). Willett and his co-workers [5] also claimed that TEG, as well as lecithin and polyoxided ethylene stearate (POES), could contribute to

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a melt viscosity reduction. However, glycerol monostearate (GMS) produced a different type of behaviour due to its complexation with amylose in starch.

2. Experimental

The wheat starch used was an unmodified pearl starch from a local starch company. Glycerin and GMS were both used as received without further purification. A linear low density polyethylene (LLDPE, NDNA 7144, MI $= 3.33 * 10^{-2}$ g/s and density $= 0.924 * 10^{3}$ kg/m^{3}), supplied by Union Carbide Corporation, was used as a reference for the flow behaviour.

Starch was dried at 70 °C for more than 24 hr prior to mixing. Dry starch, glycerin and additives were added into a temperature-controlled turbo-mixer and mixed for 5 min at ambient temperature, at a blade rotational speed of 1191 rpm. The as-processed mixtures were sealed in polyethylene bags and stored in a dry and cool place until the measurements, in attempt to eliminate any extra moisture effect on the measurements.

Thermogravimetric analysis (TGA) was conducted with a Perkin Elmer TGA-7. The operation was performed at a heating rate of 10 °C/min in presence of dry air. A sample mass of ca. $8.0 * 10^{-3}$ g was kept through the test. A typical TGA curve of the formulations is shown in Fig. 1, from which the onset temperature of decomposition T_d can be readily worked out.

Differential scanning calorimetric (DSC) analysis was performed with a Perkin Elmer DSC-7. The heating rate was 10 °C/min. The instrument calibration was done with Indium ($\Delta H = 28.6$ J/g, $T_o = 156.6$ °C) and Gallium ($\Delta H = 79.9$ J/g, $T_o = 29.8$ °C). The mixtures of ca. $1.0 * 10^{-2}$ g were weighed into stainless steel vessels, which were sealed hermetically.

Rheological measurements were carried out using a capillary rheometer, which contained a capillary with an inside diameter D of 1 mm and a length L of 5 mm, giving a L/D of 5. Three other capillaries with the same diameter but L/D values of 10, 20 and 40 were used to check for the end effects in the capillary. The measurement procedure and the consequent data processing, including the Bagley correction for the end effects and the Weissenberg - Rabinowitsch correction, followed those described in the literature [5]. Test temperatures of 150 °C, 170 °C and 190 °C were used for the formulations measured.

Tensile tests were performed with a WSM-2000 digital test machine at ambient environment (23 °C, 70% relative humidity), according to ASTM D 638-87. The standard tensile specimens were injection moulded using an SZ-60/40 injection moulding machine. The melt and the mould temperatures were kept at 175 °C and 35 °C respectively for all the mouldings. The as-processed mouldings were immediately sealed in polyethylene bags and stored at ambient temperature for more than one week prior to further tests.

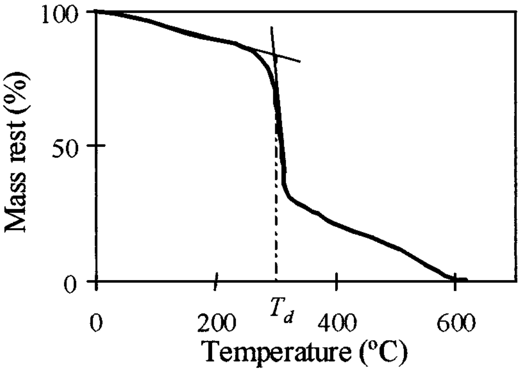


Figure 1 Determination of the onset temperature of thermodegradation T_d from a TGA trace.

A JSM-T20 scanning electron microscope (SEM) was used to examine phase morphology evolution in the extruded strands of the formulations. Fracture surfaces were prepared in liquid nitrogen. The direction of the fracture was perpendicular to the flow direction. Gold coating the fracture surfaces was implemented using a JFC-1100 ion sputter.

The environmental stability of the tensile specimens in an environmental chamber (30 °C, 90% relative humidity) was measured by weight gain. The moisture sorption was only nominated to the weight on the dry base.

3. Results and discussion

Great care has been taken while preparing and testing the formulation to minimise the moisture effect on the measurements.

3.1. Glycerin effect

Incorporation of glycerin can significantly lower the melting temperature, as well as modify the melting behaviour of starch crystallites (Fig. 2), which is similar to the water effect on starch melting [16]. The peak temperature of melting transition shifts downward from 197 °C to 136 °C as GC increases from 23% to 33.3%. Decrease in the melting point T_p, as well as in the onset thermodegradation temperature T_d as GC increases can be clearly seen in Fig. 3. It is noticeable that the span

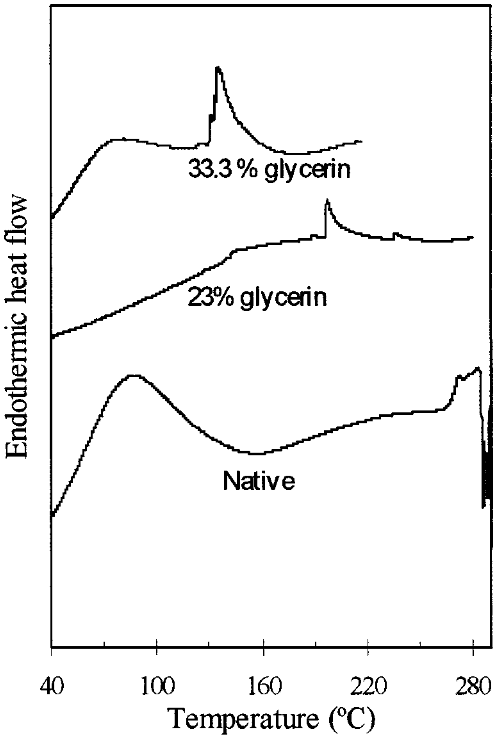


Figure 2 DSC thermograms of glycerin plasticized wheat starch.

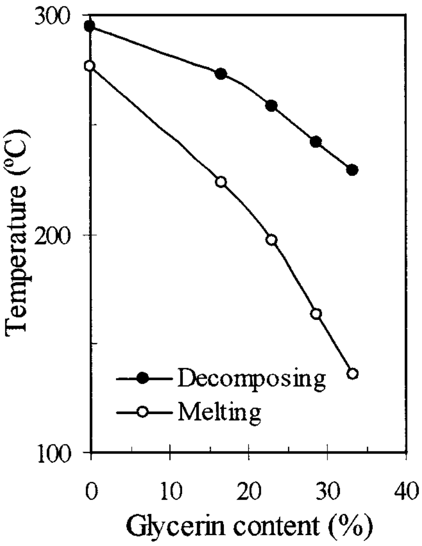


Figure 3 Glycerin effect on processing windows.

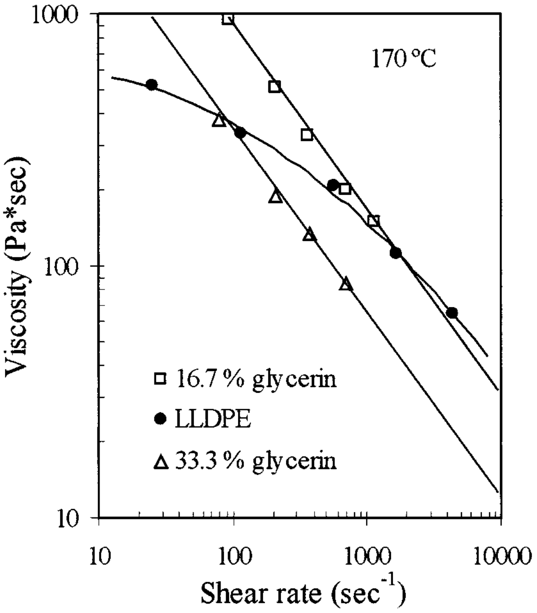


Figure 4 Melt viscosity at 170 °C of glycerin plasticized starches and LLDPE.

between T_p and T_d, coarsely representing the processing window also extends with GC. The formulation containing 33.3% glycerin can be thermoplastically processed at a temperature profile of 136–230 °C.

As a result of the plasticizer diluting effect, reduction in the TPS melt viscosity at 170 °C occurs expectedly as GC rises from 16.7% to 33.3% (Fig. 4). It is also evident that the TPS melt viscosity shows a power law dependence on shear rate. Apparently, the melt viscosity of LLDPE is intermediate between that of starch with 16.7% and 33.3% glycerin, illustrating the ability to formulate thermoplastic starches with viscosity and shear thinning characteristics similar to those of commercially available thermoplastics.

Most thermoplastics exhibit power law behaviour:

$$\eta = K\dot{\gamma}^{m-1} \quad (1)$$

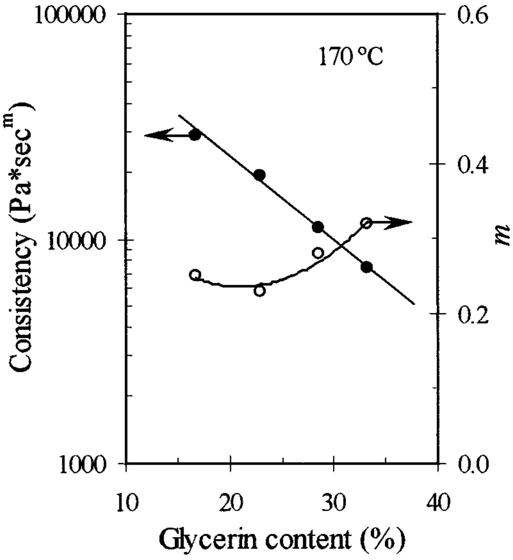


Figure 5 Effects of the glycerin content (GC) on consistency and Newtonian index.

where η is shear viscosity, $\dot{\gamma}$ is shear rate, K is the consistency and m is the power law index. Fig. 5 illustrates GC dependence of the consistency and m, derived by power law fitting of the set of flow curves at 170 °C. Obviously, GC exerts an insignificant influence on m, namely on shear thinning behaviour of TPS until it goes up to 33.3%. However, the effect of GC on reduction in the consistency is observed to follow an exponential route. Linear regression of the semilogarithmic plot of the consistency vs. GC yields a slope value of 3.6, which is much lower than those for starch plasticized by water [5]. The melt viscosity of the glycerin-plasticized starch, exponentially dependent on GC and power law dependent on shear rate, can be expressed as

$$\eta(T, \dot{\gamma}, \mathrm{GC}) = \eta_0(T)\dot{\gamma}^{m-1} \exp(-\alpha \cdot \mathrm{GC}) \quad (2)$$

where T is temperature, η_0 is the shear viscosity at zero shear rate, and α is a correlative constant.

Mechanically, increment of GC results in improvement in ductility but deterioration the tensile strength within experimental uncertainty (Fig. 6), as an expected

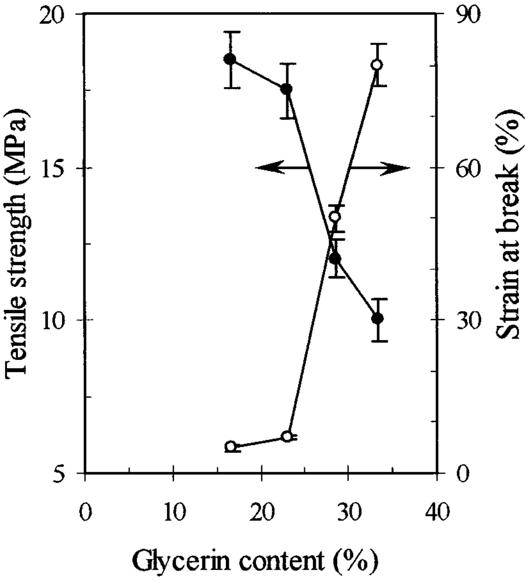


Figure 6 Glycerin effect on tensile properties.

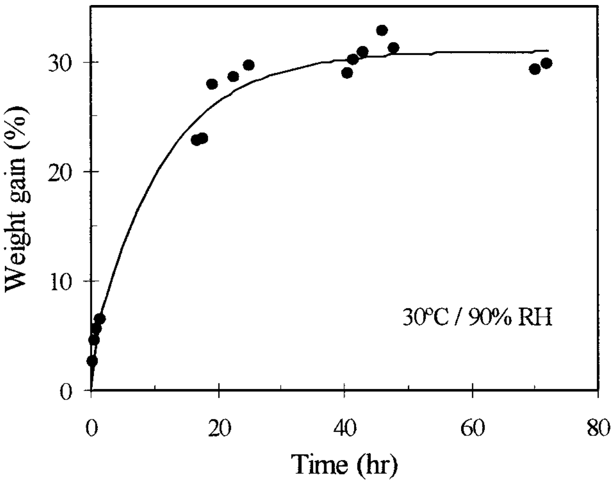


Figure 7 A typical moisture sorption curve of glycerin plasticized starch.

result of the plasticizer diluting effect. This, however, may come to the opposite if the GC used is less than 15%, the anti-plasticisation level for glycerin-starch blend [6].

A typical moisture sorption curve of the formulations is shown in Fig. 7. It is found that the data can be well fitted by an exponential function, which has been validated for other starch-based materials in our previous publication [17].

$$M = M_\infty(1 - \exp(-t/\tau)) \qquad (3)$$

where M_∞ denotes the equilibrium moisture sorption in % by weight and τ denotes the equilibrium time in hour. These two parameters derived by non-linear fitting, are linear functions of GC (Fig. 8), which can be written as

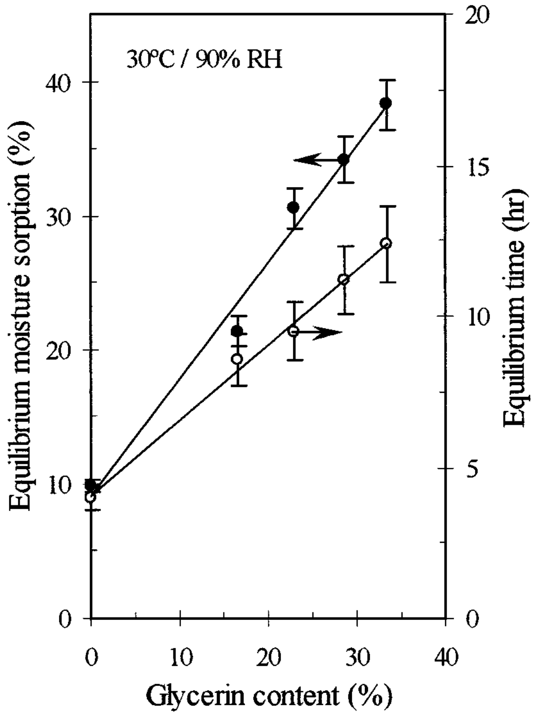


Figure 8 Effects of the glycerin content (GC) on the equilibrium moisture sorption and equilibrium time.

$$M_\infty = 9.18 + 0.87 \cdot \mathrm{GC} \qquad (4)$$

$$\tau = 4.07 + 0.25 \cdot \mathrm{GC} \qquad (5)$$

where GC is in % by weight. Combining Equations 3 through 5, one can readily determine the sorption behaviour at 30 °C and 90% RH of starch with a certain level of glycerin. However, the moisture take-up of 20% at 16.7% GC (Fig. 8) reveals a relatively strong hydration ability of the material due to the presence of glycerin. This, for a practical purpose, should be lowered to an acceptable level.

3.2. GMS effect

Normally, GMS has been used in polyolefin products as antistactic agent, mould release agent, or lubricant [18–20], and its application has recently extended in biodegradable packaging materials [21]. Effects of GMS content on the viscosity of starch containing 33.3% glycerin at various temperatures are illustrated in Fig. 9. In general, the presence of less than 2% GMS has little effects on the viscosity and shear thinning behaviour, regardless of the test temperature. However, a two-fold reduction is seen for starch containing GMS more than 2% tested at 150 °C (Fig. 9a). Fig. 9b shows a similar magnitude of reduction in viscosity for the same formulations but tested at 170 °C. Less magnitude of viscosity reduction is observed for the formulation with 2% or 3% GMS tested at 190 °C, while the formulation with 5% GMS exhibits a viscosity reduction by nearly half an order of magnitude (Fig. 9c).

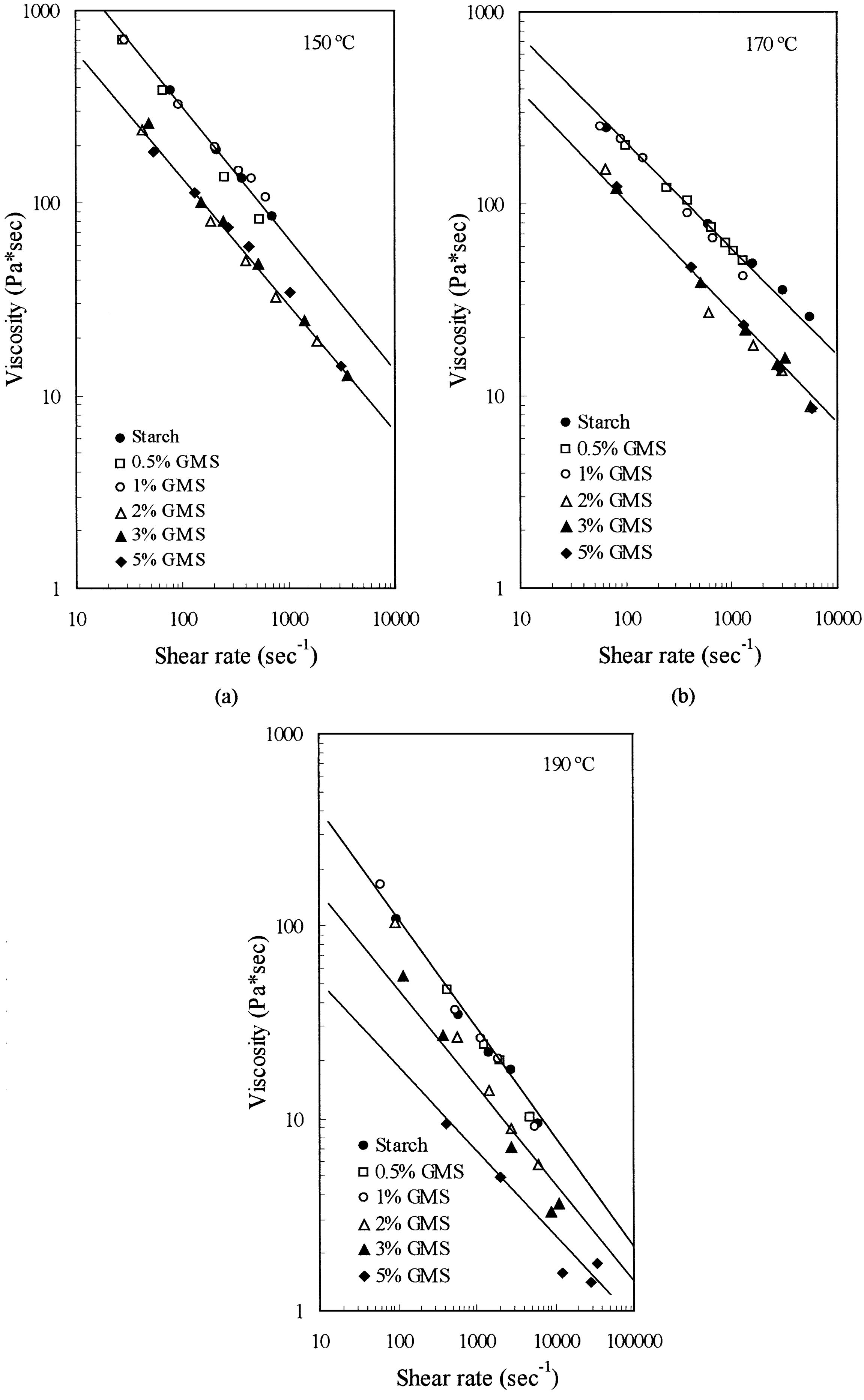
A slight decrease in m is observed for each of these sets of curves. For the formulation tested at 150 °C, m decreases from 0.36 at a GMS content of 1% to 0.31 at a GMS content of 2%. Likewise, decreases from 0.39 to 0.35 and from 0.41 to 0.37 are seen for the formulation tested at 170 °C and 190 °C respectively. These decreases are on the order of the standard error in the estimation of m by linear regression. However, a relatively large increase in m, from 0.41 to 0.57, is seen for the formulation test at 190 °C when the GMS content changes from 1% to 5%. It can thus be concluded that the GMS content of 2% is a "critical" value for the viscosity reduction of the glycerin-plasticized starch, below or above which the GMS effect can be negligible. No significant change is observed in the non-Newtonian behaviour until the formulation containing GMS greater than 5% was tested at 190 °C.

The reduction in viscosity follows the Arrhenius-type dependence of the consistency K on temperature T, which has been observed in other studies of starch rheology [5, 7]:

$$K(T) = K(T_0)\ \exp(E_a/RT) \qquad (6)$$

where T_0 is the initial temperature, R is the gas constant, and E_a is the activation energy.

Semilogarithmic plots of $K(T)$ vs. $1/T$ shown in Fig. 10 present two lines with the slopes, representing reduced activation energies (E_a/R), of 2300 and 1400 Kelvins for the control formulation (without GMS) and that with 2% GMS, respectively. These



(a)

(b)

(c)

Figure 9 Effect of the GMS content on the melt viscosity of TPS containing 33.3% glycerin (a) 150 °C (b) 170 °C (c) 190 °C.

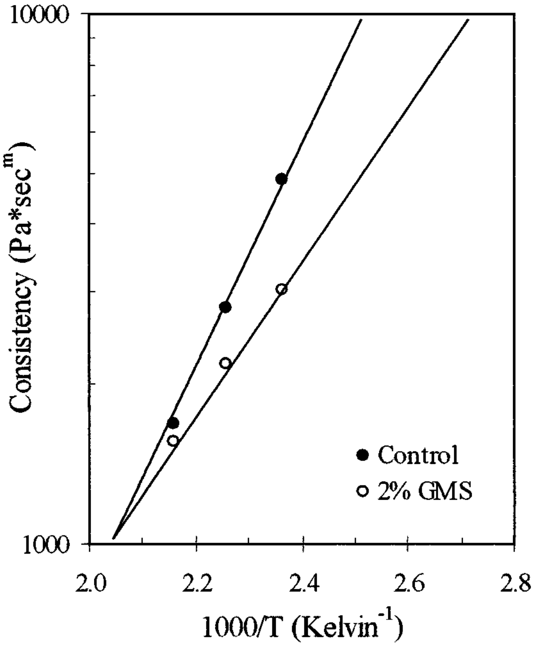


Figure 10 Relation of consistency versus $1/T$ for the control formulation and that containing 2% GMS.

values are much lower than those measured for water-plasticized starch [5]. The lower value of E_a/R for the formulation with 2% GMS reflects that the presence of GMS can efficiently enhance the temperature sensitivity of melt viscosity while reducing the viscosity and hardly affecting the non-Newtonian behaviour. This will be a great advantage for the practical thermoplastic processing of TPS in terms of ease processing and energy-input reservation.

Within experimental uncertainty, addition of GMS up to 3% has little effect on the tensile properties of the formulations, which is not illustrated for the sake of brevity. Nevertheless, the presence of GMS leads to a more than two-fold reduction in the equilibrium moisture sorption, as well as in the equilibrium time (Fig. 11), although increasing the content produces no more impact.

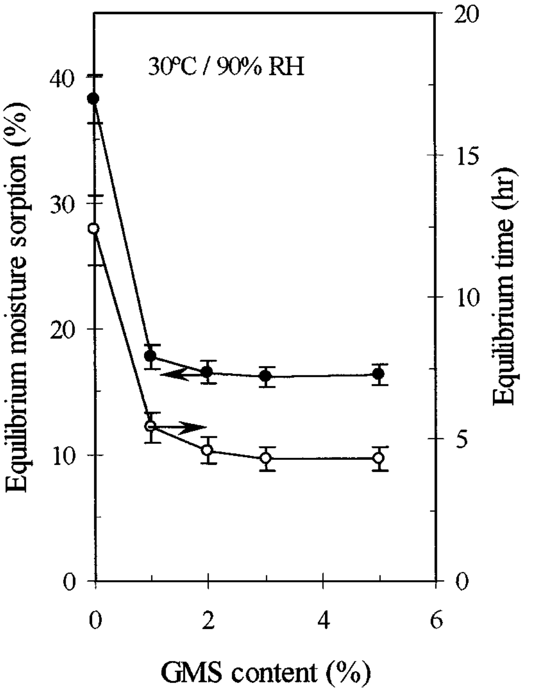


Figure 11 Effects of the GMS content on equilibrium moisture sorption and equilibrium time.

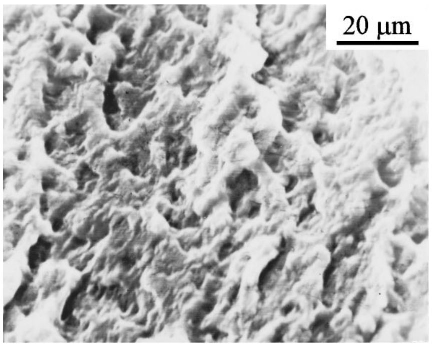


Figure 12 Micromorphology of the extrusion strand of the formulation containing 33.3% glycerin and 2% GMS.

To summarise, the formulation containing 2% GMS and 33.3% glycerin exhibits a good thermoprocessability, acceptable mechanical properties and a relatively low level of humidity sensitivity. The as-processed material shows a compact, network-textured morphology (Fig. 12). Actually, this formulation has been selected as a base material for compounding with other biopolymers, aiming at injection moulding [22].

4. Conclusions

Increasing GC leads to significant decreases in both melting point and degradation temperature of starch, and extends the range of the processing windows. Melt viscosity of the glycerin-plasticized starch is dependent on shear rate following power law, exponentially dependent on GC, and dependent on temperature in Arrhenius type. Moreover, hydration ability of the formulations increases linearly with GC. Rheologically, the presence of 2% GMS in the formulations can efficiently reduce the melt viscosity and enhance its temperature sensitivity while imposing little effect on the non-Newtonian behaviour. Furthermore, the moisture sorption of the formulations can be depressed significantly by incorporating a small amount of GMS.

Acknowledgements

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References

1. N. W. CERVONE and J. M. HARPER, *J. Food Process Eng.* **2** (1978) 83.
2. M. BHATTACHARYA and M. A. HANNA, *J. Food Technol.* **21** (1986) 167.
3. A. SENOUCI and A. C. SMITH, *Rheol. Acta* **6** (1988) 649.
4. K. L. MACKEY and R. Y. OFOLI, *J. Food Sci.* **2** (1990) 417.
5. J. L. WILLETT, B. K. JASBERG and C. L. SWANSON, *Polym. Eng. & Sci.* **2** (1995) 202.
6. D. LOURDIN, H. BIZOT and P. COLONNA, *J. Appl. Polym. Sci.* **8** (1997) 1047.
7. J. YU, S. CHEN, J. GAO, H. ZHENG, J. ZHANG and T. LIN, *Starch/Stärke* **6** (1998) 246.
8. W. AICHHOLZER and H. G. FRITZ, *Starch/Stärke* **3** (1998) 77.

9. S. H. D. HULLEMAN, F. H. P. JANSSEN and H. FEIL, *Polymer* **10** (1998) 2043.
10. P. FORSSELL, J. MIKKILA, T. SUORTTI, J. SEPPALA and K. POUTANEN, *J. Macromol. Sci. A* **5** (1996) 703.
11. J. J. G. VAN SOEST, D. DE WIT and J. F. G. VLIEGENTHART, *J. Appl. Polym. Sci.* **11** (1996) 1927.
12. J. J. G. VAN SOEST and N. KNOOREN, *J. Appl. Polym. Sci.* **7** (1997) 1411.
13. M. C. VAN DER BURGT, M. E. VAN DER WOUDE and L. P. B. M. JANSSEN, *Journal of Vinyl and Additive Technology* **2** (1996) 170.
14. J. YU, J. GAO and T. LIN, *J. Appl. Polym. Sci*. **9** (1996) 1491.
15. H. POTENTE, A. RÖCHER and B. NATROP, *Starch/Stärke* **46** (1994) 52.
16. J. J. G. VAN SOEST, PhD dissertation (Utrecht University, Utrecht, 1996) p. 43.
17. Z. Q. LIU, Y. FENG and X.-S. YI, *J. Appl. Polym. Sci.* **74** (1999) 2667.
18. J. FALTER, K. GEICK, L. HALL and J. WILLIAMS, in Proceedings of Antec’94 Conference, San Francisco, May 1994, p. 2804.
19. M. MONDRAGON, O. S. RODRIGUEZ and A. C. FLORES, *Rev. Plast. Mod.* **432** (1992) 684.
20. B. NIELSON, in Proceedings of International Conference on Additives for Polyolefins, Houston, February 1998, p. 123.
21. H. G. FRANKE and D. R. BITTNER, US 5512090 A 960430.
22. Z. Q. LIU, PhD dissertation (Zhejiang University, Hangzhou, 1998) p. 81.

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