Macromol. Symp. ***144****, 371–374 (1999)*

Effect of Additives on Gelatinization, Rheological Properties and Biodegradability of Thermoplastic Starch

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SUMMARY: Effect of additives on the starch gelatinization was governed by the processing conditions. The order-disorder transition of starch in water can occur in more than one way and the effect of polar additives on gelatinization can also be in more than one way. The additives appear to be plasticising thermoplastic starches, resulting in improving rheological properties. The thermoplastic starches with the additives are all biodegradable although the rates of biodegradability are slightly different.

INTRODUCTION: Synthetic polymers have been developed to the point where you can design microstructure and control molecular weight and molecular weight distribution. However, the mesoscopic structure within the starch granule has developed to suit the plant's own needs and is much more complex[1]. In order for thermoplastic starches to meet the requirement of processing and mechanical properties matching conventional thermoplastics various additives must be added. In this work, the effect of glycerol, urea, NaCl, KI and sugar on the gelatinization behaviour of starches under shear stress and shearless conditions were studied by DSC, WAXS and hot-stage microscope. The effect of these additives on the rheological properties was studied using a slit die rheometer attached to an extruder; and biodegradability was evaluated through composting tests.

EXPERIMENTAL: The base materials (starch and additives) used in this study are commercially available. Wheat starch (containing 12.3% moisture) from Goodman Fielder was used in this work. Gelatinization under shearless conditions was carried out in a sealed glass vial. Gelatinization under shear stress was carried out using a Haake Rheocord 90 system equipped with a Rheomix mixer.

A Perkin-Elmer Pyris-1 DSC apparatus and a Siemens D500 diffractometer WAXD were used to study gelatinization and crystallinity of starch. High shear rheology tests were

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conducted on a custom-built slit die rheometer. The biodegradability of the materials was tested by the European standard Controlled Composing Test derived from ASTM D5338092.

RESULTS AND DISCUSSION: Figure-1 shows the effect of polar additives on the gelatinization of wheat starch measured by DSC in a starch/water (70:30) system. It can be seen that the polar additives affected gelatinization temperature T_G and gelatinization endotherm ΔH_G significantly. Sodium Chloride increased the gelatinization temperature and decreased the extent of gelatinization. One possible explanation for this is that the starch acts as a weak acid ion exchanger and that cations tend to protect and to stabilize the granule structure while anions act as the gelatinizing agent by rupturing hydrogen bonds[2-5]. Sucrose also has a restrictive effect on the gelatinization process as measured by T_G and ΔH_G. This effect of sucrose is widely known and several explanations for this phenomenon have been proposed including competition between starch and sucrose for available water, sucrose inhibition of granular, and sucrose interaction[6]. On the other hand, urea enhanced the gelatinization of wheat starch through decreasing the gelatinization temperature. All the additives decreased the ΔH_G, which means the additives decreased the extent of gelatinization.

However, when the wheat starch-solution (70:30) system was treated under shear stress using the Haake Rheomix, the gelatinization endotherm disappeared, which clearly indicates that no ungelatinized starch or crystalline forms remains. It is well known that under shearless conditions, full gelatinization requires that the weight ratio of water/starch be larger than 2:1[7]. The loss of crystallinity under stress may not only be caused by the penetration of water, but also by the presence of the polar additives and mechanical disruption of the molecular inter bonds by the intense shear fields. Therefore, the water required to make the phase transition under shear stress is much lower than that required under shearless conditions. The polar additives can enhance the gelatinization under shear stress through moving into the starch granule by shear force. Under shear stress conditions, all the restrictive effects from salt and sugar have disappeared.

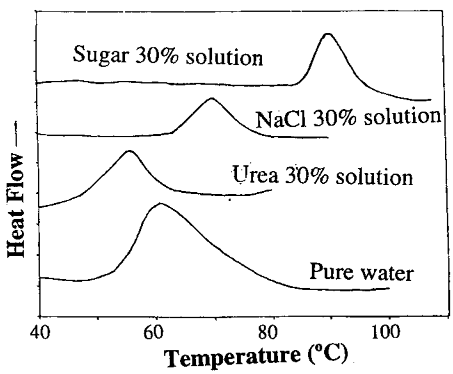

Figure-1 Effect of various additives on gelatinization temperature measured by DSC

A plot of viscosity versus shear rate for the various formulations is shown in Figure-2. It is clear that the viscosities of each of the formulations with non-aqueous gelatinising aids (urea, glycerol, sugar, KI and NaCl at 10%) are markedly lower than the viscosity of the control formulation (starch and 30% water only), although increasing the water content from 30% to 40% decreases the viscosity even further. The additives appear to be plasticising the formulations, resulting in lower processing stresses, but they are not as efficient as water. These results correspond with the date from the DSC measurement.

Figure-3 shows the biodegradability of each material measured by the compost testing. It is seen that all the samples are biodegradable, which to be expected considering that the samples are starch-based. The effect of the additives on the biodegradability is not great, but can be identified. Curve 2 and 8 show that decrease in water content has slowed down the degradation of the materials. Glycerol addition has not changed the initial rate of degradation but has slowed it down at the end of the test. On the other hand urea has increased the initial rate of biodegradation as well as overall degradation at the end of the testing period. Comparison of 7 and 8 demonstrates that addition of sugar in the starch blend has little effect on the degradation. Curve 5 and 6 show that the starch degradation has been inhibited by the addition of NaCl and KI. This is probably due to the salts affecting.

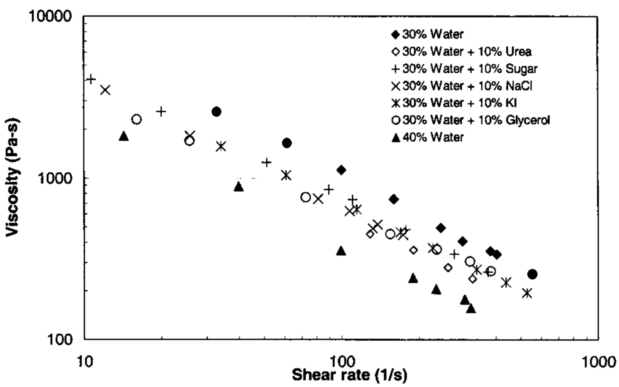

Figure-2 Shear viscosity versus shear rate for starch-based materials with 10% of various additives.

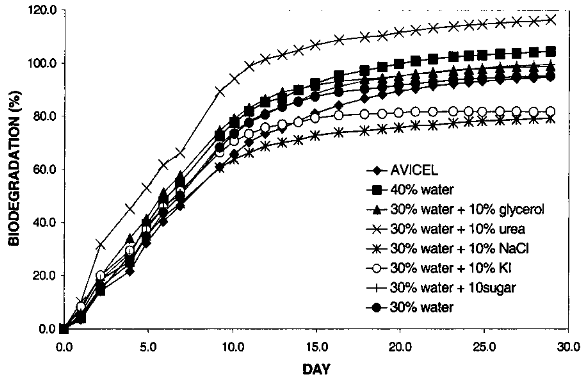

Figure-3 Biodegradability of starch-based materials with various additives.

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