Extrusion Grafting of Starch with Reactive Dyes to Form Sheets with Reduced Retrogradation

Kris Frost, Daniel Kaminski and Robert Shanks

CRC for Polymers, School of applied sciences, RMIT University, Melbourne, Victoria, Australia

Retrogradation in a high amylose thermoplastic starch film was stopped through modification with a commercial reactive dye. The resulting film had enhanced mechanical properties and greater flexibility than unmodified films. Reactive dye chemistry offers high fixation rates and may create new paths for starch modification.

1. Introduction

Thermoplastic starches (TPS) offer an excellent alternative to oil derived plastics but are still largely unable to match conventional polymers in toughness and flexibility [1]. The largest problem with TPS films to date is retrogradation. Retrogradation can be thought of as staling in foods and is a process whereby starch molecules disrupted during gelatinisation (heating in excess water) slowly re-coil into their native helical arrangements, causing TPS films to brittle rapidly [2]. Native starch helices can be either single (V type) or double helix (A and B type) and differ in molecular weight and packing arrangement [3, 4].

Starch has many hydroxyl groups that can be reacted to form modified starches. Typical reactions include acetylation and other carboxylations; etherification such as methylation, ethylation and hydroxypropylation [5]. To date the most widespread method to reduce retrogradation through starch modification is via ring-opening reactions using epoxies, creating a hydroxypropylated starch (HP). Small hydroxypropyl groups substituted onto starch alcohols prevent helical recoiling and linear regions of starch molecules aligning. The end result is a TPS film that remains flexible and has increased elongation before break [6, 7].

Reactive dyes with functionality designed to react with hydroxyl groups are available for cellulosic fibres. Typically the reactive molecules are either mono or di-chloro triazine, vinyl sulphone or fluoro-triazine based.

Reactive dyes offer an interesting method of reducing retrogradation in starch TPS. Dye chromophores may be able to stop gelatinized starch helical recoiling and alignment in much the same way as hydroxypropylation, and the reactive molecules themselves are of interest as they may provide an alternative method of starch molecular fixation other than epoxy reactions.

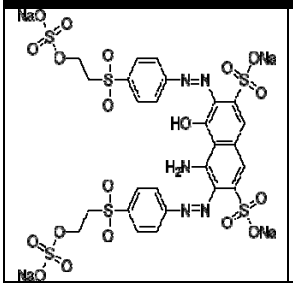
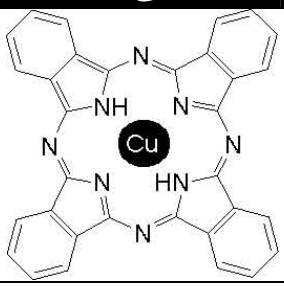
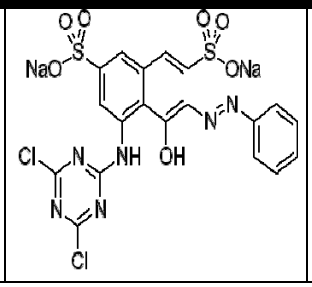
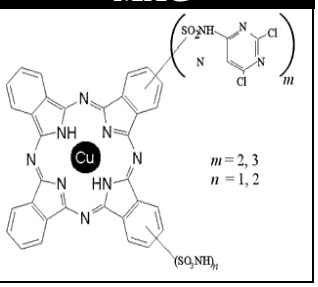
Dyes have been selected with di-chloro triazine (Procion™ MXG and MX5B) and vinyl sulphone reactive groups (Remazol™ black B and Blue G) to link the chromophore to the host molecule. The chloro-triazine groups require a stoichiometric amount of base to react with hydrogen chloride released by the reaction. The resulting salt will remain in the TPS after processing since extraction would be inefficient. Vinylsulphone is preferred because the Michael addition leaves no bi-product.

2. Method

A high amylose starch, Gelose 80, was supplied by Plantic Corporation for modification, as was a hydroxypropylated starch for comparison. Gelose 80 starch batches were hydrated in a dough mixer with a desired weight fraction of dye, and sodium hydroxide was added to catalyse the reaction. Dyes selected for trial were Procion™ MXG and MX5B and Remazol™ Black B and Blue G (Table 1). The starch dye slurry was then extruded at

95 ºC using an Axon B-12 extruder to cause the dye to react and the extrudate pelletised. Pellets were hot pressed into films using a 500 µm die at 120 ºC under 15 tons of pressure. X-ray diffraction data was collected using a Bruker D8 Discovery with GADDS attachment. All X-ray calculations were completed using Bruker TOPAS software. Stress – strain analysis was carried out on an Instron 4465 materials tester.

Table 1 – Dyes selected for starch grafting and their chemical structures

Remazol Black B	Remazol Turquoise G	Procion Red MX5B	Procion Turquoise MXG
			

3. Results

Starch / dye pellets were soxhlet extracted over a 12hour period under ethanol to extract unbound dye. The extract was then centrifuged and the resulting supernatant used for UV-Vis analysis to determine the degree of dye fixation. Results had large variability (±10%) but Vinyl-sulphone dyes (Remazol) were found to have an average fixation rate of 80% and di-chloro triazine dyes (Procion) 70%.

Films made of unmodified starch (gelose 80) were found to brittle rapidly, and x-ray diffraction studies indicated that gelose 80 TPS could be considered fully retrograded after 48 hours (Figure 1).

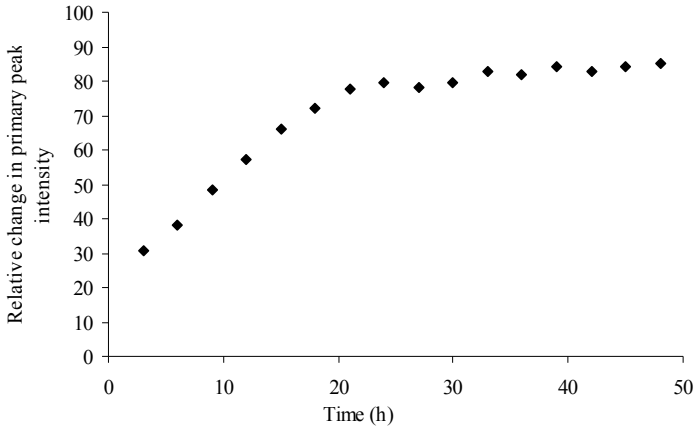


Figure 1 – Gelose 80 primary peak intensity change vs. Time

Dye modified TPS were therefore left to equilibrate over a 48 hour period before x-ray analysis (Figure 2, legend is in order of decreasing crystallinity). Gelose 80 films typically display an A type crystallographic pattern.

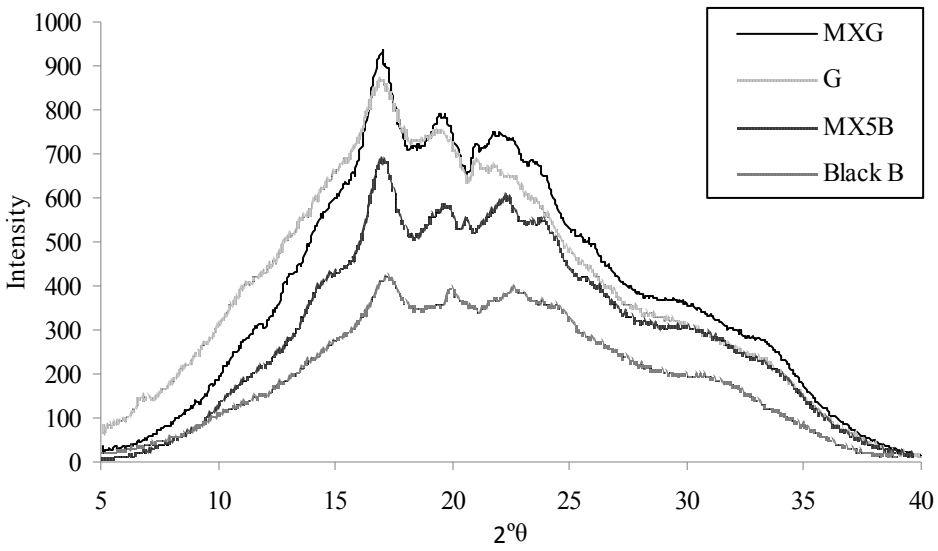


Figure 2 – X-ray analysis of retrogradation in various starch / dye TPS films at 5% w/v

X-ray diffraction patterns of Remazol black B and red MX5B showed the largest decrease in crystallinity. Gelose 80 modified with MX5B had an estimated 11% crystalline structure, followed in increasing order by Gelose 80 and Procion MX5B (14%), Remazol G (25%) and Procion MXG (28%). Crystallinity was defined as the estimated amorphous contribution divided by total spectra area and multiplied by 100 [8].

Whilst Remazol Black B provided the most reduced peak intensities and hence lowest crystallinity, the TPS it produced was brittle, even before retrogradation. This was due to its ability to act as a crosslinking agent, as the chromophore has two reactive vinyl-sulphone groups. Subsequently, Remazol black B was ignored and MX5B examined. MX5B has the smallest chromophore of the four dyes and appears to have an effect on retrogradation.

To produce a TPS with a higher degree of modification, a 25%w MX5B starch batch was created. The resulting TPS remained flexible after 48 hours of equilibration, and was observed to have similar properties to hydroxypropylated (HP) TPS films. X-ray analysis demonstrated that residual starch A and B helices (seen in gelose 80 spectra) were absent and overall structure was very similar to HP films; predominantly amorphous (Figure 3).

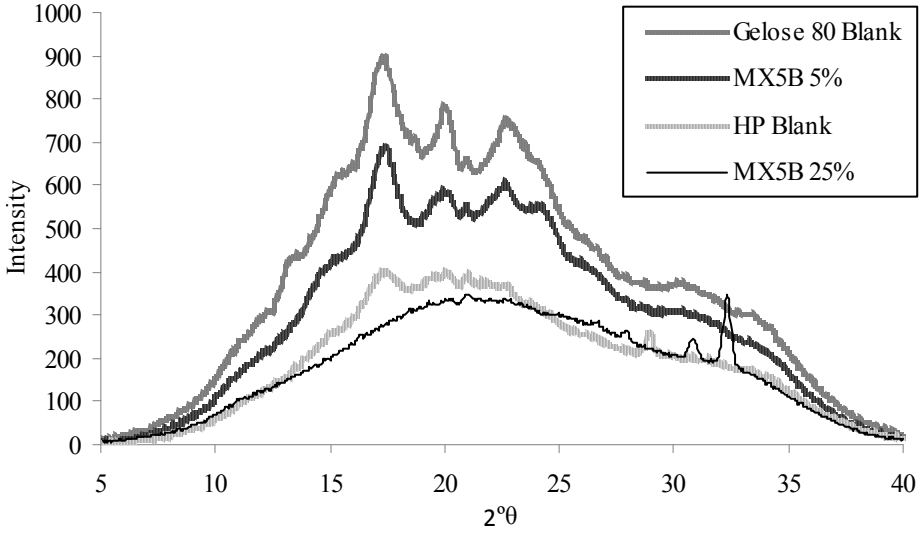


Figure 3 – Comparison of X-ray spectra for MX5B, gelose 80 and HP TPS

Mechanical testing was employed to compare the performance of MX5B TPS against gelose 80 and HP films (Table 2, Figure 4).

Table 2 – modified starch film mechanical test results

Starch modification	Modulus (MPa)	Elongation at break	Error
HP	1185	5.61	5%
G80	931	0.4	5%
5%	897	0.36	2%
25%	668	2.44	5%

The addition of MX5B at 25%w increased elongation at break and created a more viscous, flexible material.

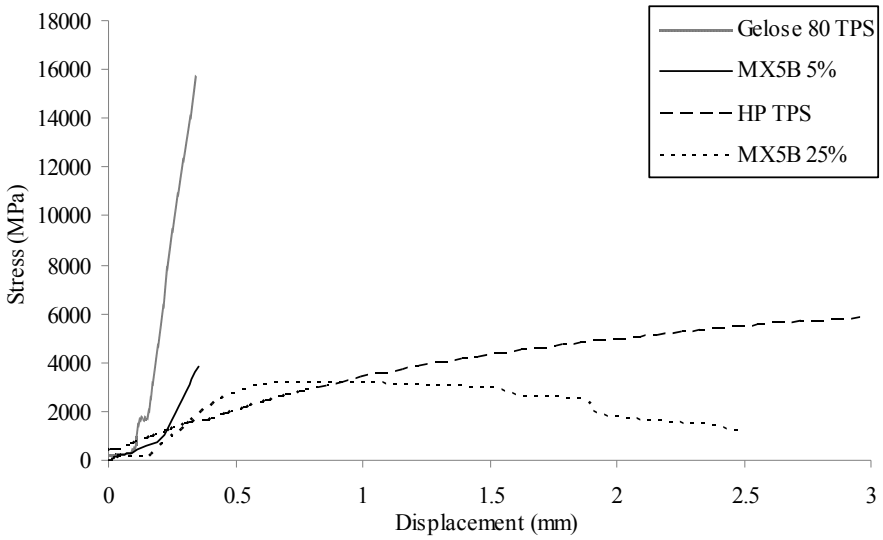


Figure 4 – comparison of MX5B, Gelose 80 and HP TPS modulus

Unlike the HP and Gelose 80 TPS, the MX5B modified starch demonstrated an ability to yield and enter into plastic deformation.

4. Conclusion

Starches modified with MX5B reactive dyes had enhanced mechanical properties over non-modified starches and different mechanical properties than hydroxypropylated starches. MX5B at 25%w was able to inhibit retrogradation, and provided a fixation rate of around 70%. Vinyl-sulphones and di-chloro triazines are suitable reactive molecules for the modification of native starches and can be implemented in reactive extrusion processes.

References

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