ARTICLES

TARTARIC ACID CROSS-LINKING OF STARCH: EFFECTS OFREACTION CONDITIONS ON THE MAXIMUM TENSILE STRENGTH OF CAST PLASTIC FILMS

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ABSTRACT:
Modification of starch by cross-linking is used in many fields, as the process improves many of the properties of starch, yet most cross-linking agents in common use tend to be toxic, expensive, or both. Polycarboxylic acids could function as nontoxic alternatives to these – some, such as tartaric acid (TA), are also less expensive. This study presents a method to cross-link thermoplastic starch films with TA, as well as the effect of this modification on the tensile strength of the material when films are prepared using different reaction conditions. An increase in strength was observed, which is believed to occur due to an increase in the London dispersion forces acting within the cross-linked starch (CLS). The greatest observed increase in the maximum tensile strength of the plastic was 6%. Monosodium tartarate was used as a catalyst for the cross-linking reaction. The maximum tensile strengths of the plastics produced were determined by using adapted binder clips, a hook (total mass 10g) and hanging masses to subject films of the plastics to progressively greater tension. Incremental weights of 10g were used, with recorded tensions at fracture of 1.2~8.9 N.

INTRODUCTION
Starch is a polysaccharide found in the amyloplasts of most green plants[1]. It is composed of amylose (linear) and amylopectin (branched) molecules, the proportions of which vary depending on the source. Cross-linking starch is the process of forming intermolecular bridges between the D-glucose units in amylose and amylopectin. This modification of starch is used for a range of food and non-food related applications. Effects appealing to the food industry include a reduction in the rate of retrogradation and resulting synereses of starch, and an increased resistance to acidic conditions, heat, shear, and an increase in the gelatinization temperature of starch[2-5]. These phenomena have been related to a reduction in the number of hydroxyl functional groups in the material and the reduced mobility of amylose and amylopectin within the amorphous phases of starch granules due to the presence of intermolecular bridges[2, 6-8]. However, the applications of cross-linked starch (CLS) are not limited to the food industry. Improvements in the resistance to dissolution in water and acidic media could allow CLS plastics to be biodegradable...
alternatives to many of the oil-based plastics commonly used in packaging\cite{9-11}. Moreover, most CLS plastics are edible, making edible packaging another possible application\cite{2}.

Most cross-linking agents currently used in the modification of starch are toxic. Nontoxic alternatives include polycarboxylic acids. These can be used to produce a safer product for use in food applications\cite{2, 6, 12}. Polycarboxylic acids cross-link through esterification reactions between hydroxyl functional groups in the D-glucose units of starch and the carboxylic acid terminal of the acids\cite{6}.

Some of these acids are of low cost, which could make them attractive in commercial environments when compared with commonly used cross-linkers such as epichlorohydrin\cite{12, 13-16}. Tartaric acid (TA) is a viable cross-linking agent for usage in the modification of starch, exhibiting similar effects on modified starch hydrogels as other cross-linking agents\cite{17}. The main positive attribute of TA is that it can be recovered from winemaking wastewater through relatively cheap processes\cite{18-28}. Approximately $8 \times 10^6$ m$^3$ of wine wastewater is produced each year in Spain - 6 times more than the wine wastewater produced in France or Italy; this represents an enormous potential supply of TA\cite{23}.

This study investigates the effect the cross-linking conditions of starch on the maximum tensile strength (MTS) of cast CLS plastic films obtained using TA as a cross-linking agent. Moreover, an optimal combination of these conditions is herein investigated such that the MTS of produced films is maximized while TA is used as the cross-linking agent. The fundamental hypothesis of this investigation is that varying these parameters will affect the MTS of solution-cast CLS plastic films.

Aqueous solutions of corn starch, glycerol TA and catalyst were used for casting. The catalyst chosen for usage was monosodium tartrate (MT), which was prepared in situ\cite{29}. The parameters considered were the weight fractions of glycerol and TA in the solution prior to casting, and the time for which the films were cured at 165°C after casting in order for the esterification reactions to take place.

### MATERIALS AND METHODS

Reagent-grade sodium carbonate, L(+) tartaric acid, and glycerol were purchased from Merck SA, Caracas, Venezuela. Distilled water was purchased from Himelab Distribuidora CA, Caracas, Venezuela. Corn starch was purchased from Citadino CA, Caracas, Venezuela.

#### Film Preparation

A solution of 0.75 mol/L TA and 0.09 mol/L MT was prepared by adding sodium carbonate to aqueous TA. This solution was used to prepare 300 mL solutions with the required concentrations of TA for the different cross-linking reactions. Starch was dispersed in these solutions as a 3% weight fraction. These dispersions were heated to and maintained at 90°C for 20 minutes on a hotplate. Afterwards, they were cooled to 60°C and the required amount of 4.89 mol/L glycerol solution was added to them. The mixtures were then stirred and poured onto polished polystyrene plates.

The mixtures air-dried at 22 ± 3 °C for 72 hours. The resulting cast films were then peeled off from the substrates before being cured in a non-fan-assisted oven at 165°C on borosilicate trays for the required amounts of time. The films were then conditioned for 48 hours at 22 ± 3 °C and 70 ± 10% relative humidity.

#### Tensile Testing

Two 10 cm by 1 cm strips were cut from each film in different directions. The MTS of each strip was determined as follows: its ends were clamped by a binder clip modified with electrical tape for improved grip. One of these clips was nailed to a shelf. A metal hook was slid through the other. Weights were loaded on this hook in 10 g increments. The load each film was subjected to at failure was used in calculating its MTS. For this calculation, the thickness of each film was measured thus: a square section of film was folded five times. The edges of this folded structure were cut off and its height was measured using a ruler precise to 0.25 mm. This height was divided by 32 to obtain the average thickness of the film. This value was used to calculate the MTS of the film. The range of measured heights was 2.75 ± 0.75 mm.
RESULTS

**Effect of Glycerol**

Glycerol is well known as a plasticizer. The glycerol percentage of a cast plastic film (with respect to the mass of starch used) has an effect on its MTS (Figure 1). Both control and cross-linked films without glycerol were too brittle to be tested. An increase in the glycerol content from 5% to 10% results in an increase of the MTS of tested films. Further increases in glycerol content cause films to exhibit progressively lower MTS values. This trend continues up to the greatest trialled content: 30%.

Qualitative observations suggest the elongation at break shown by a cross-linked starch plastic varies positively with the weight fraction of glycerol present in the same.

**Effect of Tartaric Acid**

Films cross-linked with different TA weight fractions (with respect to the mass of starch used) exhibited different MTS (Figure 2). An initial increase in TA content from 0% to 1% causes a decrease in the MTS of cast films. Further increases in TA content up to 5% bring about an increase in the films’ MTS, which reach a maximum at 12.2 ± 0.6 MPa. This represents a gain of 19.6 ± 6% in the MTS of the plastic as compared to the value measured for the film without TA. Increasing the TA weight fraction beyond 5% decreases the MTS of cast films. This trend continues through to the highest tested TA weight fraction: 15%.

**Effect of Curing Times**

The relationship between the time for which a film is cured at 165°C and its MTS was studied (Figure 3). It can be seen that there exists a range of curing times (3 to 5 minutes) where the variation in MTS is small. This is also the region where the maximum MTS was observed: for the samples that underwent 5 minutes of curing. A second set of trials was carried out for films containing 10% glycerol and 7% TA weight fractions. For these, the optimal curing time was found to be the same, with the maximum exhibited MTS being 9 MPa.

Unreacted TA that remains in the films after the curing process may function as a plasticizer. Samples cured for shorter periods exhibited more elongation at break, and greater elastic deformation throughout the progressive loading phase of the tensile test they were subject to. The deformation behaviour exhibited by a sample containing 10% glycerol and 7% TA which was not cured was remarkable in that it was very similar to that of the films containing 25% and 30% glycerol and 5% TA weight fractions, but which had been cured for 5 minutes.

Samples that were cured for 8 and 10 minutes developed a yellow colour and a smell similar to that of burnt sugar. This change in colour and smell was greater in samples that were cured for 10 minutes.

**Cross-Linking Effectiveness**

Evidence is herein presented that suggests cross-linking takes place at a significant rate with the methodology used in this study (Figure 4). It shows the MTS of a control film made of non-cured thermoplastic starch (TPS) with 10% glycerol and no TA. Figure 4 also shows the effect that curing an
identical TPS sample for 5 minutes has on its MTS. Likewise, it depicts the effect that the presence of a 5% weight fraction of TA has on the MTS of another identical sample that was not cured. Both of these are substantial reductions in the plastic’s MTS: 11.5% ± 7% and 37% ± 4% due to curing and the presence of TA respectively. However, when a TPS sample with a 5% weight fraction of TA is cured for 5 minutes, an increase of 6% ± 5% from the control film’s baseline MTS is observed.

**Effectiveness of the Catalyst Used**

Significant variation of MTS with curing time was observed for samples containing TA. This suggests the rate of the esterification reaction during curing was significant. Hence, a mass of monosodium tartrate equal to 13.8% of the used TA mass would be effective as a catalyst for the cross-linking of starch when TA is used as a cross-linking agent.

**Figure 3:**

*The optimal curing time is 5 minutes.* Maximum tensile strength tests were carried out on samples synthesized with a 10% glycerol weight fraction and a 5% tartaric acid weight fraction that were cured for different periods of time. Two strips were cut from each film and tested in random directions and their average maximum tensile strength was calculated. Error bars are shown. The relationship between the average maximum tensile strength of these films and the time for which they were cured is depicted.

**Figure 4:**

*A comparison of maximum tensile strengths suggests cross-Linking took place under the used conditions.* Maximum tensile strength tests were carried out on four samples (A, B, C, D) all of which had 10% glycerol weight fractions. Neither sample A nor B had tartaric acid weight fractions. Sample B was cured for 5 minutes while sample A was not cured. Samples C and D both had 5% tartaric acid weight fractions, but sample D was cured for 5 minutes while sample C wasn’t cured.
**Optimal Synthesis Parameters:**

The optimal conditions used during cross-linking to obtain films with the largest MTS were found to be: Weight fractions of 10% and 5% of glycerol and TA respectively, and a curing time of 5 minutes. This combination yielded a CLS plastic film of a MTS of 12.2 ± 0.6 MPa.

**DISCUSSION**

The way the reaction conditions affect the MTS of cast films can be explained through theories proposed in existing research. In these, the mobility and molecular weight of the constituent molecules of CLS is given importance.

**Glycerol and TA as Plasticisers**

The results show that adding glycerol to CLS initially increases its MTS, but further additions result in a drop in MTS. This could be explained by a progressive increase in the mobility of the CLS molecules – where this is caused by an increased distance between these, resulting from having the plasticizers embed between CLS molecules and forming hydrogen bonds with their hydroxyl terminals. It must be noted that not all hydroxyl functional groups in amylose and amylopectin act as sites of esterification during the curing process, and hence remain hydroxyls in CLS [17].

It is possible that a small number of plasticizer molecules provide CLS molecules with enough mobility to rearrange when subject to stress. The macroscopic effect of this would be the exhibition of elastic and plastic deformation [30, 31]. However, an excess of plasticizers could separate CLS molecules to a point where the intermolecular forces they experience are significantly reduced. This could cause a reduction in the MTS of the material [6, 32, 33].

The elongations at break of the tested films were qualitatively recorded as comparative observations while the MTS tests were carried out. However, existing research shows that glycerol content increases the elongation at break of CLS films using a similar polycarboxylic acid as the cross-linking agent [6]. The usage of glycerol and polycarboxylic acids as plasticisers in other bioplastic systems is well documented [30-34].

**The Presence of Cross-Links**

Figures 2 and 3 suggest that increases in the number of cross-links in CLS initially increase its MTS. This could be due to an increase in the London dispersion forces (LDFs) in the material: if amylose and amylopectin molecules became cross-linked, their resulting molecular weight would be larger. Hence, the LDFs experienced by CLS molecules should be greater than those experienced by amylose and amylopectin in native starch. This could increase the MTS of the macroscopic material.

Figure 3 also suggests that excessive cross-links have a negative effect on the MTS of CLS. This could be attributed to cross-linked molecules having less mobility than unmodified amylose and amylopectin.

**Curing Weakens Films**

This study corroborates that curing will degrade TPS, weakening films and producing changes in colour [6]. Also, films were conditioned for 48 hours after being cured as otherwise; they were too brittle to be tested. This could be attributed to evaporation of water in the films during curing since water also has a plasticizer effect. If so, after the water present in a film has evaporated during curing, its amylose, amylopectin and CLS molecules would be heated at a greater rate and hence degrade more quickly. This might explain the very low MTS of films that were cured for 8 and 10 minutes.

**CONCLUSION**

This analysis proposes that a critical degree of mobility must be reached in CLS for its MTS to be maximized. The optimal set of reaction conditions balances the converse effects of cross-links and plasticizers on the mobility of CLS molecules while keeping their LDFs as large as possible. At the same time, these conditions must minimize the thermal degradation to the material during curing.

**FUTURE DIRECTIONS**

While the present study explores the ways the MTS of CLS made with TA is affected by the reaction conditions used, there remains a range of this material’s properties that have not been studied herein.

It would be of interest to investigate the reduced solubility of TA-CLS in acidic conditions, since this is...
typically one of the improvements of cross-linking on thermoplastic starch\(^6\). Likewise, the thermal properties, Young’s modulus, yield behaviour, permeability and morphology of these films could be investigated.

The effectiveness of catalysts other than monosodium tartrate when TA is used could be further investigated. Many are expected to be effective\(^{29, 35, 36}\).

The processability of CLS plastics (TA-based or otherwise) has not been investigated in detail. However, it would be of interest to determine the effects of cross-links in this regard, since this is a very important material characteristic in industry.

**ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tr>
<td>TA</td>
<td>Tartaric Acid</td>
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<td>CLS</td>
<td>Cross-Linked Starch</td>
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<tr>
<td>MTS</td>
<td>Maximum Tensile Strength</td>
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<td>MT</td>
<td>Monosodium Tartrate</td>
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