Tensile stress and elongation properties of edible plastics from starch

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Edible grade plastics have been developed by thermal extrusion of mixtures containing starch (major ingredient) and glycerol and water as plasticisers in different relative proportions. The product made from a mixture containing 69% starch, 18% glycerol and 13% water optimally gave a tensile strength of about 10 N/mm² and an elongation of 10%. Gradual replacement of starch from this optimum mixture by addition of corresponding amounts of gelatin showed a gradual reduction in tensile strength of the products while % elongation followed an irregular increasing trend up to the use of about 18% gelatin. Improvement in mechanical property was possible by incorporating cellulose into starch-gelatin mixture containing optimum dose levels of glycerol and water.

Widespread use of disposable and non-biodegradable plastics poses a great threat to the mankind. Development of eco-friendly substitute is being sought worldwide basically through blending synthetic polymers with starch following different techniques¹,². In such formulations, starch has been used either in the granular³, thermoplastic⁴ or gelatinised⁵ form to produce various disposable items. However, the claim for biodegradability of these products leads to confusion since only the starch portion gets readily degraded leaving the synthetic counterparts intact for years⁶,⁷. Till date, development of true biodegradable plastics with desirable properties remains a challenge. Use of natural biopolymers as the sole source of raw materials could be a suitable proposition in this aspect. In addition, if the biopolymers are of edible grade, the prepared plastic could be considered as a part of food or feed.

Recently several reports⁸⁻¹¹ have been documented on production and quality assessment of films or coatings consisting of edible grade polysaccharides, proteins and lipids, either alone or in combination. Such materials are to be used for preservation or quality improvement of fresh, frozen or fabricated food or for encapsulation of flavours and pharmaceuticals. These films or coatings may be consumed along with the items. Therefore, for the edible grade natural polymers to be used as plastics for disposable articles or films, it is necessary that proper blends are to be prepared and their mechanical properties to be studied as one of the primary requisites.

The objective of this work is to produce plastics by extrusion technology using different proportions of edible polymers namely starch (major ingredient), gelatin and cellulose, followed by evaluation of their tensile strength and elongation properties.

Experimental Procedure

Desired proportions of corn starch (commercial grade, purchased from local market), cellulose powder (laboratory grade, SD fine chem. ltd.) and gelatin (laboratory grade, Loba chemie), and the plasticisers like glycerol (laboratory grade, Ranbaxy laboratories ltd.) and water (glass distilled) were combined and mixed together in a mixer (Sumeet, model no. SP16 electronic) for 5 min. The mixture was then extruded in a single screw extruder (Brabender, Germany) using the particular screw of compression ratio 1:1. To ensure complete gelatinisation of starch and to avoid overcooking, the temperatures of the feed,
mixing and metering zones of the extruder were maintained at 70, 110 and 110°C, respectively. The temperatures and the screw compression ratio used for extrusion were as recommended by the manufacturer of the extruder unit. Desiring to obtain the products with appreciable mechanical strength, extrusion of any feed mix was carried out at a screw speed of 60 rpm as reported by Swanson et al. in case of plastics from starch and synthetic polymers. To maintain a steady flow of extrudate, the feed hopper screw speed was synchronised at 20 rpm. The extrudates, given the form of rod using a 3 mm diameter die, were collected on a tray kept in ambient condition. The materials were prone to microbial growth (because of presence of moisture) if stored as such and, therefore, were subjected to drying (usually after every 15 min of collection) in an air oven at 40 ± 1°C for 24 h under very low air circulation rate. This condition of drying was found to be adequate to arrest the microbial growth as well as any stress crack development. As there is a usual time gap between the manufacture of plastics and their use, and the properties of natural polymers are likely to change on ageing, the products were kept in open mouth polythene sachets and stored inside a room at an ambient condition for about 7-9 months (for exposure to variable weather) i.e., in a condition simulating the normal storing condition for plastic made disposable articles. The stored products were equilibrated at 50% relative humidity for 48 h (ASTM D638-71a) and then the stress-strain properties, under tensile force, were measured as followed by Swanson et al. using Instron Universal Testing Machine (Instron, UK). The measurement was done in 10 replicates for each composition. Average values along with the standard errors of ultimate tensile strength (UTS) and elongation at break (EL) are reported in the present discussion.

### Results and Discussion

In the extruder, starch granules get compressed, get deformed and start to melt and lose their crystalline regions. As the material passes through the shear zone, moisture and friction heat in combination with external heat contributes to gelatinisation (plasticisation), while the hydrogen bonds in native starch molecules disaggregate and mobile water diffuses to form hydrogen bonds with the hydroxyl groups of the anhydrous glucose units available in the polymer chain. In case of glycerol plasticisation also, similar hydrogen bonds develop between the polar hydroxyl groups of glycerol and those of the starch replacing the original starch-starch hydrogen bonds. Plasticisation decreases the cohesive force and rigidity of native starch along with an increase in chain pliability and the starch molecules align themselves along the stream lines in the laminar flow occurring in the extruder screw and die. Plasticisation is manifested in decreased UTS and increased elongation of the finished material. Table 1 shows the UTS and elongation at break of the rod-like products made from different mixtures containing 69% corn starch and different amounts of glycerol and water. The product made without any glycerol and with only water as the additive for corn starch indicated an UTS of 12.35 N/mm² and an elongation of 4.17%. With increase in the glycerol content in the mixture and corresponding lowering in water content, the UTS gradually decreased while the per cent elongation increased. Interestingly, when the product was finally made using 31% glycerol without any added water, there was a lowering in per cent elongation.

In spite of expected good plasticising effect of water on starch during processing, the highest UTS and lowest elongation of the product made from these two ingredients may be due to loss of moisture during post extrusion drying and storage destroying the starch-water bonding and restoring the association of starch molecules (starch-starch bonding) through the formation of new intra- and inter-chain hydrogen bonds, and ultimately inhibiting chain pliability. Thus, water alone is not a suitable plasticiser for getting a product with appreciable flexibility. While using a mixture of glycerol and water, both these ingredients form hydrogen bonds with starch; however, unlike water, glycerol content will remain unaltered.

### Table 1—Ultimate tensile strength and elongation of products made from mixtures containing water, glycerol and starch

<table>
<thead>
<tr>
<th>Composition (%)</th>
<th>UTS N/mm²</th>
<th>EL %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch</td>
<td>Glycerol</td>
<td>Water</td>
</tr>
<tr>
<td>69</td>
<td>9</td>
<td>22</td>
</tr>
<tr>
<td>69</td>
<td>18</td>
<td>13</td>
</tr>
<tr>
<td>69</td>
<td>24</td>
<td>7</td>
</tr>
<tr>
<td>69</td>
<td>31</td>
<td>7</td>
</tr>
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</table>
during drying and storage and hence the bond between glycerol and starch in the product will remain stable. Gradual increase in the amount of glycerol replacing the water, therefore, gradually impaired the original starch-starch interaction in the way of more and more stable starch-glycerol hydrogen bonding i.e., contributing more and more plasticisation. Probably these lead the extrudates for having less UTS and high elongation. However the cause for less elongation of the product containing glycerol (31%) as the only plasticiser, compared to that of the product containing 24% glycerol and 7% water (Table 1), was not apparent within the experimental limit. It may be pertinent to mention that reduction in both the UTS and elongation due to increase in glycerol (used as plasticiser) concentration from 16 to 30% was also reported by Coffin and Fishman21 in case of edible films from pectin and starch.

The results in Table 1 reveal that the product made from 69% starch, 18% glycerol and 13% water gives appreciable UTS (≈ 10 N/mm²) and elongation (≈ 10%); these values are also found to be comparable to those of non-edible and biodegradable products containing corn starch, poly(ethylene-co-acrylic acid) and polyethylene reported by other workers13. This composition has been considered as the optimum for blends containing starch, glycerol and water.

Increase in gelatin concentration (0.0-22.0%) into the above mentioned optimum mix, replacing an equal amount of starch caused a gradual reduction in UTS of the extrudates (Table 2). However, the variation in per cent elongation did not follow any particular trend. For addition of gelatin from 0 to 7%, the elongation of the products increased from 10.07% (no gelatin) to 34.15%; with respective addition of 11% and 15%, the elongation values were 24.86% and 27.93%. A sharp increase in per cent elongation (27.93-50.11%) was noticed when the gelatin content of the mix was raised from 15 to 18%. However, very peculiar behaviour was obtained with increase in gelatin content beyond 18%. For use of 20% gelatin, there was a steep fall in per cent elongation, while the change in UTS was just nominal (Table 2). When gelatin content was further increased by 2%, a sharp decrease in UTS of the product occurred (1.47 to 0.43 N/mm², 70.74% decrease) with a marginal (~11%) drop in per cent elongation. From the above results in Table 2, it appears that if the gelatin content in the blend is more than 20%, the product strength will be too low to sustain an elongation more than about 10%.

Like starch, gelatin, a random coiled protein, is also plasticised by water and glycerol19,24. Mixing and thermal extrusion of blends containing gelatin and starch along with the plasticiser probably facilitates this protein to undergo interaction with starch25-27, over and above the 'usual polymer-plasticiser hydrogen bonding. Since the molecular weight of gelatin is less than that of starch19,28, the resultant starch-gelatin complex will have lower molecular weight compared to that of starch19. Thus, increasing amount of gelatin in the mix may gradually reduce the molecular weight of the starch-gelatin mixture resulting in a gradual reduction in UTS. Decrease in UTS with increasing amount of casein in pectin-casein edible film was also reported by Parris et al.29. Park et al.30 observed that UTS of films made from cellulose-derivatives decreased with decrease in molecular weight of the polymers. When subjected to stretching, the increased product elongation is attributed primarily to the uncoiling of the gelatin. However, the cause of fluctuating elongation trend of the product above 7% gelatin content is obscure, probably this random coiled protein imparts a steric effect at the high gelatin: starch ratio, or this may be due to unpredictable nature of the anticipated starch-protein complex. It is worth mentioning here that all the products made from starch, gelatin, glycerol and water were re-extrudable indicating a thermoplastic nature.

The effect of cellulose on the tensile properties of the products was studied in a blend containing

<table>
<thead>
<tr>
<th>Percentage of</th>
<th>UTS</th>
<th>EL</th>
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<tbody>
<tr>
<td>Starch</td>
<td>Gelatin</td>
<td></td>
</tr>
<tr>
<td>69</td>
<td>0</td>
<td>10.0±0.28</td>
</tr>
<tr>
<td>65</td>
<td>4</td>
<td>4.37±0.17</td>
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<tr>
<td>62</td>
<td>7</td>
<td>4.20±0.16</td>
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<tr>
<td>58</td>
<td>11</td>
<td>3.51±0.09</td>
</tr>
<tr>
<td>54</td>
<td>15</td>
<td>2.11±0.11</td>
</tr>
<tr>
<td>51</td>
<td>18</td>
<td>1.57±0.09</td>
</tr>
<tr>
<td>49</td>
<td>20</td>
<td>1.47±0.08</td>
</tr>
<tr>
<td>47</td>
<td>22</td>
<td>0.43±0.04</td>
</tr>
</tbody>
</table>

*Glycerol – 18% and water – 13%
49% starch and 20% gelatin, keeping the plasticisers at the optimum level. Table 3 shows the results. It is apparent from the table that, replacement of 5% starch by the same quantity of cellulose increases both the UTS (84.35% increase) and elongation (65.88% increase) values, compared to that of the product without cellulose. Improved stress of the products containing cellulose might be attributed to the highly organised crystalline structure of this polysaccharide; and on this basis, increase in elongation of the extrudates is an interesting observation. However, on 20% supplementation, the UTS and elongation values slightly decreased from the preceding one. May be that this large quantity of fibrous material imposed a physical heterogeneity to such an extent that it could not produce any beneficial effects over and above the 5% addition.

**Conclusion**

Proper concentration of glycerol and water in starch has been found to impart desirable plasticising effect in moderating the tensile strength and elongation of the extrudates. Replacement of starch by gelatin in an optimum starch-glycerol-water formulation increased the elongation with a corresponding decrease in tensile strength of the products. Cellulose, when incorporated in these blends, was found to improve the stress-strain properties of the developed plastics. This study is continuing for investigating the effects of various edible ingredients on the properties of the newly developed plastics with respect to their optimisation.

**References**