Effect of Plasticizer on the Properties of Pellets Made from Agro-Industrial Wastes

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ABSTRACT
Extruded pellets were made based on deoiled rice bran and paddy husk using glycerol and cashew nut shell liquid as plasticizer. Effects of incorporation levels of glycerol (GL, 6 to 14%) and cashew nut shell liquid (CNSL, 6 to 14%) on the physical and functional characteristics of extruded pellets based on deoiled rice bran and paddy husk powders were studied. For A3 samples (12% GL) radial expansion (RE-1.052), bulk density (BD-0.697 g/cm³), water solubility index (WSI-13.000%), water binding capacity (WBC -5.237%) and hardness (HD-498.253 N) were observed. However, in case of B3 samples (12% CNSL), radial expansion (RE-1.019), bulk density (BD-0.567 g/cm³), water solubility index (WSI-15.037 %), water binding capacity (WBC-4.785) and hardness (HD- 495.027 N) were observed. Results indicated that GL and CNSL had a significant effect on physical and functional properties of the pellets. The results suggest that deoiled rice bran and paddy husk powder can be plasticized with glycerol and cashew nut shell liquid for the development of durable pellets using extrusion technology to be used further for the development of biodegradable molded pots.

General Terms
Biodegradable pellets, extrusion, injection molding.

Keywords
Cashew nut shell liquid, Glycerol, physical and functional properties.

1. INTRODUCTION
Extrusion cooking as a continuous mixing, cooking and forming process, is a low cost, versatile, and efficient technology in food processing. The raw materials during extrusion undergo chemical and structural transformations, such as starch gelatinization, protein denaturation, complex formation between amylose and lipids, and degradation reactions of vitamins, pigments, etc. [1]. Extrusion has found its application in other sectors like packaging technology (pellets for film and molded product development) besides being used for the development of food products. The properties of materials during extrusion are modified due to physico-chemical changes of the biopolymers due to the thermal energy generated by viscous dissipation during extrusion, combined with shearing effect [2]. Over the last two decades, polymers from renewable resources have attracted an increasing amount of attention due to two major reasons: firstly environmental concerns, and secondly the realization that our petroleum resources are finite. Generally, polymers from renewable resources contain natural polymers, such as protein, starch and cellulose. The demand for inexpensive sources of protein, which can be used as a value added products is increasing in recent years [3]. Protein has attracted much attention as one of the important renewable and abundant resources in the field of packaging due to its biodegradability [4]. Deoiled Rice bran (DOB) is a valuable source of such inexpensive protein, contains about 12-20% protein [5] and is an underutilized agro industrial by-product [6]. Proteins are linked via substituted amide bonds forming a highly complex polymer. Due its complexity in composition and structure, proteins possess multiple functional properties; such as gelation, solubility, emulsification, elasticity and cohesion-adhesion [7]. Damodaran [8] reported that protein has an ability to interact with neighbouring molecules and form a strong cohesive, viscoelastic sheets and composites that can withstand thermal and mechanical motions [9]. Manisha [10] developed extruded pellets with proteins isolated from deoiled Rice Bran for the development of biodegradable molded sheets and determined the effect of glycerol on the properties of the sheet.

Paddy husk is also one of the major agricultural residues containing cellulose in similar amounts with wood [11]. Usually paddy husk has been a problem for rice farmers due to its resistance to difficult digestion, decomposition in the ground, inadequate final disposal (burning) and low nutritional value for animals [12,13]. According to Martiferrer [14] the hemicellulose and lignin contents of paddy husk are lower than wood. For this reason paddy husk can be processed at higher temperatures than wood. Therefore, the use of paddy husk in the manufacture of biodegradable pellets using extrusion technology is attracting much attention. Simone [12] has successfully developed biodegradable thermoplastics composites by melt extrusion using paddy husk flour as filler and found that density of composites slightly increased with filler. Yang [15, 16, 17] in various studies observed that tensile and impact strengths decreased with increasing filler loading while the elastic modulus increased in case of paddy husk composites. Han [18] determined the possibility of using lignocellulosic materials as reinforcing fillers in the thermoplastic polymer composite, and found that paddy husk could be utilized as biodegradable filler in polymeric materials to minimize environmental pollution.

In view of the vast availability of these two types of by-products and waste materials: extruded pellets were developed and characterized. Moreover, no research till date has been published on pellets developed from these two biodegradable agro industrial wastes using GL and CNSL as plasticizer. Hence, the main aim was to study the aspects related to the effect of the different types of plasticizer on the properties of the pellets and to establish correlations between these properties.

2. MATERIALS AND METHODS
2.1. Procurement of raw material
Deoiled rice bran (DOB) used for the present study was kindly donated by M/s. AP Solvex Ltd., Dhuri (Punjab, India) which contain high level of protein. Glycerol, used as a reference plasticizer in this study was of analytical grade (M/s. Merck Specialities Pvt. Ltd., Mumbai, India). Other plasticizer used in this study was CNSL which was kindly donated by M/s. Allen Petrochemicals Pvt Lt., Meerut (India). Paddy husk (PDH) was also provided from M/s. AP Solvex Ltd., Dhuri. Paddy husk and DOB was ground in a Laboratory grinding mill (M/s. Philips India Limited, Kolkata, India) and passed through screen (80 mesh) to obtain fine powder.

2.2. Extrusion process for the preparation of Pellets
In the blend preparation, DOB, PDH, CNSL and GL were used. Different formulations used for different samples are tabulated in Table. 1. The moisture was adjusted to 10%. All the ingredients were weighed and then mixed in a Hobart mixer (M/s. Continental Equipment India Pvt. Ltd, Delhi, India) for 20 min at 328 rpm using sigmoid shape blade. This mixture was then passed through an 80 mesh sieve to prevent the lump formation due to addition of moisture. After mixing, samples were stored in polyethylene bags at room temperature for 24h.

Extrusion was performed using a co-rotating twin-screw extruder (M/s. Basic Technology Pvt. Ltd., Kolkata, India). Screw speed was set at 277 rpm and extrusion was done for different samples. The specific mechanical energy (SME) of extrusion was calculated as

\[ \text{SME} = (\omega/\omega_\text{c}) \times (\tau/100) \times (Z_\text{r},Q) \]  

where \( \omega \) is screw speed, \( \omega_\text{c} \) is the rated screw speed, \( \tau \) is percent torque, \( Z_\text{r} \) is rated power and \( Q \) is the feed rate. Screw speed was set at 277 rpm, feed rate at 107.5 g/min, barrel temperature at 110°C and rated power was 4755.75 hp.

Table 1. Formulations and specific mechanical energy of the pellets

<table>
<thead>
<tr>
<th>Code</th>
<th>DOB (%)</th>
<th>PDH (%)</th>
<th>GL (%)</th>
<th>Water (%)</th>
<th>SME kJ/Kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>50</td>
<td>50</td>
<td>6</td>
<td>10</td>
<td>89.047</td>
</tr>
<tr>
<td>A2</td>
<td>50</td>
<td>50</td>
<td>10</td>
<td>10</td>
<td>110.513</td>
</tr>
<tr>
<td>A3</td>
<td>50</td>
<td>50</td>
<td>12</td>
<td>10</td>
<td>128.363</td>
</tr>
<tr>
<td>A4</td>
<td>50</td>
<td>50</td>
<td>14</td>
<td>10</td>
<td>138.086</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Code</th>
<th>DOB (%)</th>
<th>PDH (%)</th>
<th>CNSL (%)</th>
<th>Water (%)</th>
<th>SME kJ/Kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>50</td>
<td>50</td>
<td>6</td>
<td>10</td>
<td>81.310</td>
</tr>
<tr>
<td>B2</td>
<td>50</td>
<td>50</td>
<td>10</td>
<td>10</td>
<td>106.767</td>
</tr>
<tr>
<td>B3</td>
<td>50</td>
<td>50</td>
<td>12</td>
<td>10</td>
<td>120.822</td>
</tr>
<tr>
<td>B4</td>
<td>50</td>
<td>50</td>
<td>14</td>
<td>10</td>
<td>131.853</td>
</tr>
</tbody>
</table>

2.3. Radial expansion
The ratio of diameter of extruded pellet and the diameter of die was used to express the radial expansion of extruded pellet [19]. The diameter of extruded pellets was determined as the mean of 10 random measurements made with a Vernier calliper. The radial expansion ratio was calculated using the following formula:

\[ \text{Radial Expansion ratio} = \text{Extrudate diameter/die diameter} \]  

2.4. Bulk density (BD)
Bulk density was calculated according to the method of Alvarez [20]. Cylindrical pellets were filled to a volume of 30 ml Filling was randomly done by selecting bulk of pellets which were poured from a height of approximately 100 mm from the brim of the cylinder.

\[ BD (g/ml) = \frac{m}{V} \]  

Where \( m \) is the bulk density, \( m \) is mass (g) of pellets with \( v \) is the volume of the pellets filled.

2.5. Static coefficient of friction (COF) and Angle of repose (AR)
The static coefficient of friction and angle of repose was calculated according to the method of Maurice [21]. The static coefficient of friction (\( \mu \)) is calculated from the following equation:

\[ \mu = \tan \alpha \]  

The angle of repose is derived from the following equation:

\[ \theta = \tan^{-1}(2H/D) \]  

Where, \( H \) and \( D \) are the height and diameter of the heap, respectively.

2.6. Water binding capacity (WBC) and water solubility index (WSI)
Water binding capacity (WBC) and WSI were estimated as per the method described by Anderson [22].

\[ \text{WBC} = \text{weight of the sediment/weight of dry solid} \times 100 \]  

\[ \text{WSI} = \text{weight of dissolved solids in supernatant/weight of dry solids} \times 100 \]

2.7. Hardness
Texture profile analysis (TPA) of all the extruded puffs was performed in triplicate using Texture analyzer (TA-X2i, Stable Microsoft System, UK). Hardness (N) of the samples was recorded by analysing the TPA graph using the Texture Exponent 32 software (Stable Microsoft system, UK). Hardness was determined by placing five pellets from each sample on the platform of the analyzer with a probe SMS – P75 – 75mm diameter at a crosshead speed of 2 mm/sec with a target mode of 2 mm distance. The compression generates a curve with the force over distance. The highest first peak value was recorded as this value indicated the first rupture of pellet at one point and this value of force was taken as a measurement for hardness [23].

2.8. Statistical analysis
Statistical analysis was conducted using a commercial statistical package, Design-Expert version 6.0.10 (Stat-Ease Inc., Minneapolis, USA). The analyses of extruded samples were conducted in triplicates.

3. RESULTS AND DISCUSSION
The proximate analysis of raw materials revealed that DOB contained moisture content 8.08 %, ash 8.42 %, protein 14.6 %, fat 0.67 %, crude fibre 8.75 % and carbohydrates 59.48%. PDH contained moisture content 9.41 %, ash 12.82 %, protein 0 %, fat 0 %, crude fibre 25.33 % and carbohydrates 52.44 %.
3.1 Specific mechanical energy (SME)
As shown in Table 1, the increase of SME implies the increase in viscosity of composite melt which can be attributed to the increase in the plasticizer content in the formulations. A hypothetical reason for the maximum torque at increased glycerol content may be the plasticizing effect of the plasticizers at elevated levels in the first stage and an exposure of hydrophilic sites, reinforcing the cross linkage. Thereafter, the network structure might be formed with covalent crosslinks and that the molecular size is reduced due to the increasing mechanical shear. Similar effects were observed for SME by Andreas [25] wherein they reported lowest SME for lowest glycerol content.

3.2 Radial expansion (RE)
The range of expansion was between 1.087 to 1.025 in case of (A) samples and 1.058 to 1.018 for (B) samples (Table 2). It was observed that expansion decreased with the increase in the amount of plasticizer for both the samples (A and B) this behaviour can be attributed to the increased binding properties of the plasticizers with the particles at elevated levels. Moreover, this behaviour can also be attributed to the effect of the temperature and shear on the expansion of the pellets [26]. Another reason may be due to the amount of high protein content in DOB and high fiber contents in paddy husk. Proteins affect the RE through their ability to influence water distribution in the matrix and through their macromolecular structure that affects the extensional properties of the extruded melts [26]. Onwulata and co-workers [27] investigated the effects of whey protein concentrate and isolate on the characteristics of biodegradable pellets which indicates that the extruded biodegradable pellets bear a good compaction and in turn a dense product [34]. Good compaction may be due to the plasticizers used for binding purpose. Highest value was observed for A4 (0.597 g/ml) and B4 (0.595 g/ml). Lowest values were observed in sample A1 (0.567 g/ml) and B1 (0.439 g/ml).

3.3 Water solubility index (WSI)
In this experiment the WSI ranged from 17.120 to 20.880 % for (A) samples and 16.270 to 19.542 % for (B) samples (Table 2). There was an inverse relation of the water binding capacity and the water solubility index of the pellets and pots. William [28] also shows that water solubility index is inversely proportional to water absorption index. It was also observed for both the cases that there was a significant rise in the WSI with the increase of the plasticizer upto 10% which then reduces for sample A3 and B3 this behaviour can be attributed to the binding effect of the plasticizer at the particular percentage.

3.4 Water binding capacity (WBC)
The increase in the amount of plasticizers (from 6 to 14%) increases water binding capacity from 4.785 to 6.355 % in case of ‘A’ samples and 3.395 to 4.795% for B samples. This behaviour may be attributed to the hygroscopic nature of the plasticizer (Table 2). The hydrophilic and hygroscopic nature of the plasticizers actually forms the large hydrodynamic plasticizer-water complex [32]. Another reason may be due to the presence of fiber and protein in PDH and DOB respectively. The water absorption is the characteristic feature of fiber supplemented powders as reported by several researchers [29, 30]. Fibre may interact with water by means of polar and hydrophobic interactions, hydrogen bonding and enclosure. The results of these interactions vary with the flexibility of the fiber surface [31]. Moreover, number of hydroxyl group which exist in the fibre structure is mainly caused by water, allowing absorption and interaction through hydrogen bonding [33].

<table>
<thead>
<tr>
<th>Table 2. Effect of plasticizer on functional properties of pellets</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Functional Properties of Formulations</strong></td>
</tr>
<tr>
<td><strong>WBC (%)</strong></td>
</tr>
<tr>
<td>A1</td>
</tr>
<tr>
<td>4.785±0.11</td>
</tr>
</tbody>
</table>

All the values are Mean ± SD. WBC: water binding capacity, WSI: water solubility index, RE: radial expansion

3.4 Bulk density (BD)
The density of extrudates varied between 0.567 to 0.597 g/ml for (A). However, for B samples observed results in the range of 0.439 to 0.595 g/ml (Table 2). There is an obvious increase of bulk densities of biodegradable pellets which indicates that the extruded biodegradable pellets bear a good compaction and in turn a dense product [34]. Good compaction may be due to the plasticizers used for binding purpose. Highest value was observed for A4 (0.597 g/ml) and B4 (0.595 g/ml). Lowest values were observed in sample A1 (0.567 g/ml) and B1 (0.439 g/ml).

3.5 Static coefficient of friction (COF) and Angle of repose (AR)
The static coefficient of friction on stainless steel for both the samples decreased with the increase in plasticizer level as shown in Table 3. As the plasticizer increases surface of the pellets becomes smoother and in turn apply less friction towards the surface. Correa [35] reported similar results for rice grains applying less friction onto the surfaces. The angle of repose (Table 3) for both the samples did not show significant change but there was an decrease in the values upon increasing the amount of plasticizer. The parameter is important in proper design of hoppers to maintain continuous flow of the pellets, which must be larger than the pellet’s angle of repose.

3.6 Hardness (HD)
The range of HD was found to be in between 439.805 to 460.897 N for A samples and 392.454 to 487.044 N for B samples (Table 1). For HD the increase in the plasticizer amount showed a significant effect on pellets. This could be attributed to the lower expansion of products leading to increased HD as observed from expansion values, due to increased binding effects of plasticizer and high protein/fiber in DOB and PDH. As proteins affect the RE through their ability to influence water distribution in the matrix and through their macromolecular structure and conformation that affects the extensional properties of the extruded melts [26].
Table 3 Effect of plasticizer on physical properties of pellets

<table>
<thead>
<tr>
<th>Physical Properties of Formulations</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>A4</th>
</tr>
</thead>
<tbody>
<tr>
<td>BD (g/ml)</td>
<td>0.567±0.019</td>
<td>0.587±0.009</td>
<td>0.697±0.43</td>
<td>0.597±0.010</td>
</tr>
<tr>
<td>B1</td>
<td>0.439±0.002</td>
<td>0.562±0.111</td>
<td>0.576±0.43</td>
<td>0.595±0.018</td>
</tr>
<tr>
<td>A1</td>
<td>439.805±0.02</td>
<td>448.583±0.1</td>
<td>6</td>
<td>498.253±1.6</td>
</tr>
<tr>
<td>B1</td>
<td>392.454±0.14</td>
<td>448.592±0.0</td>
<td>5</td>
<td>495.027±0.15</td>
</tr>
<tr>
<td>A1</td>
<td>0.613±0.05</td>
<td>0.597±0.01</td>
<td>0.522±0.01</td>
<td>0.454±0.07</td>
</tr>
<tr>
<td>B1</td>
<td>0.574±0.02</td>
<td>0.568±0.07</td>
<td>0.561±0.05</td>
<td>0.555±0.01</td>
</tr>
<tr>
<td>A1</td>
<td>25.641±0.01</td>
<td>38.2340.01</td>
<td>45.000±0.05</td>
<td>46.397±0.01</td>
</tr>
<tr>
<td>B1</td>
<td>33.690±0.06</td>
<td>36.607±0.01</td>
<td>37.117±0.02</td>
<td>43.452±0.02</td>
</tr>
</tbody>
</table>

All the values are Mean ± SD
BD: bulk density, HD: hardness, COF: coefficient of friction, AR: angle of repose

4. CONCLUSION
The responses for pellets include RE, BD, WSI, WAI and hardness were affected by both GL and CNSL. It was concluded that the studies on the properties of the biodegradable pellets and ingredients used for their production can be helpful in designing of equipments for further processing of these pellets (injection molding). Based on the observed bulk densities it was seen that extruded biodegradable pellets bear a good compaction. The studied properties affected the compactness of the pellets would help in improving the effective storage of pellets which in turn improves the product quality. Amount of plasticizer and extrusion temperature showed significant effect on functional and physical properties. The findings of this study investigated the feasibility of developing value added products (pots) from mixture of DOB and PDH with in combination GL and CNSL by extrusion processing.

5. ACKNOWLEDGMENT
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6. REFERENCES


