Mathematical Modelling of Thin Layer Drying Kinetics of Biodegradable Pellets

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Abstract
The deoiled rice bran, industrial waste (paddy husk, potato peels and banana peels) and plasticizers were added to develop pellets after extrusion for their further use in preparing molds (pots) for horticultural use. Pellets were prepared by extrusion technology using glycerol and cashew nut shell liquid as plasticizers and were dried in a chamber with constant air circulation (1.5 m/sec). Drying kinetics of pellets made from different formulations was studied at different temperatures (60, 70 and 80°C). In declining rate period, moisture transfer from pellets was described by applying 12 different mathematical models, and the corresponding rate constants (k) were calculated. The models in each case were finally selected to explain the drying behaviour based on Chi-square, RMSE and R2. Results indicated that removal of moisture from these pellets was rapid in initial hours and increased with increase in temperature as well. The effect of temperature on rate constant (k) was interpreted according to Arrhenius law. Drying rate and hence, k values were found to be significantly affected by temperature. The energy value increased upon increasing the plasticizer concentration (CNSL and Glycerol) in the formulation. Also, the energy required in the drying of pellets with CNSL as a plasticizer was higher as compared to those with the glycerol.

Keywords: Deoiled rice bran; Paddy husk; Potato peels; Banana peels; Cashew nut shell liquid

Introduction
Nursery owners or growers use pots and cell trays of different materials, sizes, shapes, and colours to suit crop species, growing methods, and marketing strategies [1]. At nurseries and greenhouses, seeds, bulbs, and young plants are planted in cell trays or pots containing growing substrate to start the growth under uniform cultivation conditions. However, one of the limitations of impermeable and rigid containers is that roots tend to encircle the outer perimeter of the pot which results in reduced plant growth, health, and survival once transplanted [2]. Most of the containers used for transplanting are made of non-renewable oil-based raw materials such as polystyrene, polyethylene and polypropylene with suitable mechanical properties, chemical and microbial degradation resistance as well as durability. But at the same time disposal and recycling process of post-use plastic products determine their uncontrolled combustion with the subsequent emission of toxic substances both into the atmosphere and into the soil. Hence, a valid alternative to the employment of petroleum based thermoplastic pots may be represented by the use of biodegradable pots [1-5]. Once buried, the biodegradable pots are subjected to biodegradation process, being transformed in biomass and inorganic products. Now, the attention is being focussed on the development of novel biodegradable and cost-competitive pots or multiple nurseries. These pots are bio-composites whose continuous phase is characterized by biopolymers coming from renewable and available origin, such as polysaccharides [6,7] and whose solid phase, dispersed within the polymeric matrix, is represented by natural fillers and fibres coming from wastes of agro-food and textile processing industries [8]. There is a substantial interest in replacing some or all of the synthetic plastics by biodegradable polymers in several applications. Industrial production of pellets by extrusion process for manufacture of biodegradable products is relatively new and therefore the effectiveness of the availability of pellets rely upon understanding the storage stability of these pellets. A novel kind of low cost, biodegradable and medium water-resistant composite from corn protein was developed by Wu et al. [4], wherein glycerol-plasticized pots showed good biodegradability and promising water resistance [8].

The thermal energy generated by viscous dissipation during extrusion combines with the shearing effect. Several studies have reported chemical changes during extrusion cooking and related them to product functional qualities e.g. expansion volume, water solubility and color [4,9].

In order to study the consequences of the drying on the pellets it’s necessary to possess a deep data of the mass transfer parameters and also the drying kinetics. The mathematical models have been established to be helpful in the new design and/or improvement of drying systems and analysis of mass transfer phenomena concerned throughout drying [10]. The optimal control of a drying process is thus critical and needs complete information regarding the drying behaviour of materials. Drying kinetics may be described using the transport properties such as thermal conductivity, thermal diffusivity, moisture diffusivity as well as interface heat and mass transfer coefficients [11].

Previous research is available on the dilatometry studies of phosphotungstic acid pellets during hydration and dehydration processes [12]. Bassene et al. [13] performed thin layer drying kinetics of pellets prepared from millet flour at different drying air temperatures and found that modified Henderson and Pabis was the best model to describe the behaviour of pellets from millet flour. Since literature is scanty on the drying behavior/ characteristics of pellets used for development of biodegradable products, the present study was undertaken to describe the drying mechanism of pellets.
developed from different industrial byproducts, wastes and plasticizers at different drying temperatures.

The objectives of the present study are:

- To study the applicability of several mathematical models selected from literature to the drying of biodegradable pellets of different formulations
- To fit the drying data into the most suitable models by appropriate regression analysis in order to investigate the best model for describing the drying characteristics of the pellets.

Materials and Methods

Procurement of raw material

Deoiled rice bran used for the present study was kindly donated by M/s. AP Solvex Ltd., Dhuri (Punjab, India) which contain high level of protein helpful for binding of material to other ingredients. Glycerol was 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 cashew nut shell liquid kindly donated by M/s. Allen Petrochemicals Pvt. Ltd., Meerut (India). Paddy husk was also provided from M/s. AP Solvex Ltd., Dhuri (Punjab, India) for 20 min at 328 rpm using sigmoid shape blade. This mixture was then passed through an 80 mesh sieve to eliminate the lumps formed due to addition of moisture. After mixing, samples were stored in airtight HDPE plastic packs for further use.

Sample preparation

Preparation of banana and potato peel powder: Paddy husk was ground in a Laboratory grinding mill (M/s. Philips India Limited, Kolkata, India) and passed through 60 mesh screen to obtain fine powder. Banana peels and potato peels were procured locally from local juice vendors and Hostel Mess as well as Canteen, respectively.

Extrusion process for the preparation of pellets

In the blend preparation, ingredients like deoiled rice bran, paddy husk powder, potato peel powder, banana peel powder, cashew nut shell liquid and glycerol were used at levels shown in Table 1. The moisture was adjusted by sprinkling the distilled water on all the dry ingredients. 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 eliminate the lumps formed 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). The twin screw extruder was kept running for suitable period of time to stabilize the set temperatures and samples were then fed in to feed hopper at the feed rate of 4 kg/h for easy and non-choking operation. Screw speed was set at 125 rpm and the suitable quantity of water was added to makeup the moisture content to 10%. The horizontal split design of the extruder allowed the collection of samples inside the extruder channel with a ‘dead-stop’ run. Samples were taken along the extruder channel and made into pellets using suitable die and high speed cutter. The pellets had on average about 7% moisture content. The preliminary experiments carried out to study the moisture isotherms (unpublished) showed that the pellets being hygroscopic absorbed moisture to about 30% in different storage conditions. This required drying of pellets to suitable moisture content before using injection moulding to prepare pots.

Drying kinetics of pellets

The drying experiments carried out in a tray dryer (M/s. Balaji Enterprises, Saharanpur, India) at selected three air drying temperatures (60, 70 and 80°C) to study the drying characteristics of the pellets. The drying cabinet was equipped with an electrical heater, a fan, and temperature indicators. Air velocity was set at 1.5 m/s. When the dryer reached steady state conditions (i.e. when desired temperature was reached) the pellets were spread onto the trays. Moisture loss was recorded at every 15 min intervals during drying. Drying was continued until the moisture content of the sample reached to the equilibrium moisture content. The drying was continued till weight became constant. The experiments were conducted in duplicates.

Drying kinetics model

Various types of mathematical models have been used to describe drying of pellets, ranging from theoretical models based on classical diffusion theory and simplified forms of these to purely empirical models as shown in Table 1.

Statistical evaluation

The results obtained were statistically evaluated using Excel worksheet of MS office version 2010 (MS Office) and Statistica-log software package version 7 (StatSoft Inc., OK, USA). The regression analysis was performed using the STATISTICA computer program. Nonlinear regression, which used to evaluate goodness of fit of the mathematical models to the experimental data are coefficient of determination (R²), the reduced chi-square (χ²) and % Root Mean Square Error (RMSE) was used for data analysis and calculated as below:

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^{N} (\text{MR}_{\text{Experimental Value}} - \text{MR}_{\text{Predicted Value}})^2}{N}}$$

$$\chi^2 = \sum_{i=1}^{N} \frac{(\text{MR}_{\text{Experimental Value}} - \text{MR}_{\text{Predicted Value}})^2}{(N-n)}$$
Results and Discussion

Drying rate

The variation of moisture content with drying time is obtained for each sample made from different formulations. From these results, drying rates were calculated and then plotted against time. Plots of MR against drying time showed a linear relationship as shown in representative graphs in Figure 1, which indicates that the entire drying curve can be represented approximately by a diffusion model. In all the cases, the drying rate decreased continuously throughout the drying period. The drying took place in the falling rate period. Similar type of observation was reported by Singh et al. [14] wherein the drying rate of sweet potato slices decreased continuously throughout the drying period.

Selection of drying models

The convective drying of biological materials in the falling rate period is diffusion controlled process and may be represented by Fick’s second law of diffusion. Different types of mathematical models have been used to describe drying of foodstuffs, ranging from theoretical to purely empirical models [15]. The drying data were converted to moisture ratios which were then fitted to twelve drying models at these to purely empirical models [15]. The drying data were converted to moisture ratios which were then fitted to twelve drying models.
temperatures 60, 70 and 80°C and the parameters for validation of different equations were shown in Table 2. The higher value for $R^2$ and the lower values for $\chi^2$ and RMSE indicated the better fitness of model Togrul [16], and the best model based on lowest RMSE and $\chi^2$ values as well as highest $R^2$ were shown in Table 2 for each formulation.

The results reveal that the best mathematical model for sample A160 is Midilli when $R^2$ is 0.999 where the model equation is $MR = a\exp(-\frac{E}{RT}) + bt$ and the parameters are described in Table 2. For different samples, values of $R^2$ are obtained in the range of 0.969 to 1.000. Similar type of results was also reported by Augusta et al. [17] wherein they have determined the highest $R^2=0.983$ and lowest $\chi^2=0.002$ for drying of cork planks. The lowest $\chi^2$ values for different samples also determine the best fit of the models as in case of B160, the value of $\chi^2$ is 0.004. For other samples, the range of the $\chi^2$ is in between 0.001 to 0.709. Bassene et al. [13] have reported the similar results of $\chi^2$ for drying of millet flour pellets. For all cases, lowest values of RMSE are in between 0.001 to 0.082%.

**Effect of temperature variables on drying characteristics**

The results suggested that the Arrhenius law might be applicable to relate the dependence of the rate constant on drying air temperature. The relationship is given by the following equation:

$$k = k_0 \exp\left(-\frac{E}{RT}\right)$$

The computed values for activation energy for pellets are shown in Table 3. As evident that the energy required for drying of pellets containing CNSL is more than that of those pellets which contain glycerol as plasticizer. Moreover, it was also seen that the activation energy increased with the increase in the concentration of the CNSL. The dependence of the rate constant on drying air temperatures and types of plasticizers (glycerol and CNSL) are shown in representative graphs as in Figure 2.

**Conclusion**

In this study, drying kinetics of pellets were studied at drying air temperatures of 60, 70 and 80°C using a constant air velocity of 1.5 m/s. Mathematical modelling allowed the estimation of drying parameters and different models were found fit for different samples of pellets made from different formulations. It was found that drying rate took place in the falling rate period. The drying rate constant was related to temperature using the Arrhenius relationship. It would be possible to attain faster drying with increased drying temperature up to 80°C with reduced time. It was also seen that the drying energy increased with increasing amount of CNSL in the pellets and the pellets made with glycerol took less energy than that of those made from CNSL.

**References**