17th International Drying Symposium (IDS 2010)
Magdeburg, Germany, 3-6 October 2010

WATER SORPTION BEHAVIOUR OF EXTRUDED CASSAVA BIOPLASTICS ADDED OF CO-PRODUCTS OF BIODIESEL INDUSTRY

J.A. Ruano Ortiz[1], C.Y. Takeiti[2], C.W.P. Carvalho[2], J.L. Ascheri[2], A.P.S. Minguita[2], F.S. Barbosa[3]

[1]*Departamento de Ciência e Tecnologia de Alimentos, Universidade Federal Rural do Rio de Janeiro (UFRRJ)*
Rodovia BR 465, km 7 Seropédica CEP: 23.890-000, Rio de Janeiro-RJ, Brazil,
Tel+(55)(21) 3787-3750 - Ramal 246, E-mail: ruano.juan@gmail.com

[2]*Embrapa Food Technology*
Av. das Américas, 29501, Guaratiba, CEP 23020-470, Rio de Janeiro - RJ, Brazil
Tel+(55) (21) 3622-9796, E-mails: cristina@ctaa.embrapa.br, cwpiler@ctaa.embrapa.br, ascheri@ctaa.embrapa.br, paloma@ctaa.embrapa.br

[3]*Departamento de Química, Universidade Federal Rural do Rio de Janeiro(UFRRJ)*
Rodovia BR 465, km 7 Seropédica CEP: 23.890-000, Rio de Janeiro-RJ, Brazil,
Tel+(55)(21) 3787-3750, E-mail: fabio.dsbmail@yahoo.com.br

Abstract: This work comparatively studied the water adsorption and stability of cassava flour extruded with different concentration of micronized castor bean cake and sunflower cake powder and glycerol by extrusion under the same operational parameters. The water adsorption isotherms were determined by using the gravimetric method. The samples were placed in varied relative humidity (RH) environments. The experimental data were well adjusted to the GAB isothermal. The experimental data showed that the extruded bioplastics were less hygroscope than those of non mixture. According to GAB isothermal model, the bio-plastics can be safely stored from 58 to 70% RH and temperature of 25°C.

Keywords: extrusion, cassava, co-product, bioplastic production.

INTRODUCTION

Huge quantities of synthetic plastic are used in the modern life. As a consequence of this massive use, the environment has been greatly affected. Eco-friendly alternatives, such as the called bioplastic has been considered to alleviate the pollution caused by non-easily biodegradable petroleum based plastics upon the environment. Starch is probably the most abundant and cheapest of the commercially available natural polymer followed by the co-products resulted from the industrialization of the biodiesel that can be used in the bioplastic production.

There is a global concern in searching packaging materials which could both protect properly food products and has little impact in the environment. Among raw materials, natural polymers (starch and protein), plasticizers (glycerol) and reinforced materials (cakes) of by-products of renewable fuels industry can be use in film and coating production.

Cassava is a root found in tropical regions that has to be processed into starch and flour forms since it perishes quickly. Considering cassava flour, some fibers and proteins are kept in the final product, when compared to the starch form.

Extrusion technology has been widely used to produce a large variety of starch bioplastics. This process combines heat, shearing and pressure, resulting in the gelatinization of granular starch, denaturation of protein and formation of complexes among starch, lipids and proteins (Camire et al., 1990). Starch under conditions mentioned above and in the presence of plasticizer, bioplastic can be produced.

Biodiesel industry produces a lot of quantities of by-products such as cakes (residues of oil extraction) and glycerol (coproduct of esterification reaction). These components can be use as a reinforced material (cakes) as well as plasticizer (glycerol) in the bioplastic production in order to improve their mechanical properties (Muller et al., 2009).

Understanding the water sorption behaviour of bioplastic can conduce to predictive informations about its stability and it also contributes in the investigation of structural features of films, such as specific surface area, pore size distribution, crystallinity and consequently, it can affect directly the processing, handling, packing and storage.

Considering the importance of varying the composition (reinforced material contents) in order to improve the stability and the commercial application of extruded bioplastics, this work comparatively studied the sorption isotherm measurement of cassava flour with different concentration of micronized castor cake and sunflower cake powder (0.5, 1, 2, 2.5, 5 and 10%) at 28% water content and 8% of glycerol.

MATERIALS AND METHODS

Materials

Cassava flour, donated by Embrapa Genetic Resources and Biotechnology (Brazil), was used as starch source. The chemical composition of the cassava flour was 88.75% carbohydrates, 0.9% proteins, 0.56% fat, 3.48% ash, and 6.31% moisture.

The micronized castor bean cake and sunflower cake were donated by Embrapa Agroenergy, Brazil. Both course materials were finely ground in a planetary ball mill Fritsch (Idar-Oberstein, Germany) for 60 min in order to produce micronized powder of average particle size of 20 µm. The chemical composition of the micronized castor bean cake was 44.76% carbohydrates, 36.18% proteins, 2.75% fat, 9.77% ash, and 6.54% moisture.

Preparation of extruded bioplastics

The sample of cassava flour with different concentration of micronized castor cake and sunflower cake powder was equilibrated to 28% of moisture and 8% of glycerol.

Moisture processing of samples was calculated in terms of the initial moisture of the mixture. 2g of each sample was weighted in an infrared balance (MOC 120H, Shimadzu, Japan) and dried at 105° C until constant weight (Instituto Adolfo Lutz, 1985). The amount of water to be added was calculated according to Equation 1:

$$Y = \left[\frac{(Xf - Xi)\, x\, W}{100 - Xf} \right] \quad (1)$$

Where:

Y = amount of water to be added (ml)

Xf = final moisture content of the sample (%)

Xi = initial moisture of the sample (%)

W = weight of sample (g)

After adjusting moisture, the samples were homogenized manually, and then stored in plastic bags for approximately -18°C for 24 hours to allow the uniform distribution of water. Only after this conditioning period, each batch (500g) was submitted to the extrusion process.

Extrusion

Cassava flour added with different charge contents and glycerol was submitted to a Brabender DSE 20 (Duisburg, Germany) single screw extruder (Figure 1) under the same operational parameters: temperatures at the 1st, 2nd and 3rd heating zone: 50, 80 and 100ºC, respectively; screw compression ratio (3:1); laminar die of 1 mm and rotational screw speed at 180 rpm. The experiment studied the effect of seven levels of micronized castor bean cake and sunflower cake (from 0,5, 1, 2, 2.5, 5 and 10%), resulting in 12 treatments.

Figure 1. Digital photography of Brabender DSE 20 single screw extruder.

Sorption isotherm

Samples were stored in a sealed container at 25°C in the presence of saturated salt solutions (NaOH, $MgCl_2 6H_2O$, NaBr, NaCl, KCl and H_2O) of known water activities (a_w) (0.372, 0.462, 0.538, 0.712, 0.788, 0.974) and were weighed periodically until the equilibrium moisture. The samples placed at 0,788 and 0.9744 of aw presented mold growth, thus, the experiment terminated when the weight loss became lower than 2% per 12 hours (usually two to three days).The results were converted to isotherms by taking the final moisture content of each step and plotting it against relative humidity.
The isotherm data were fitted by a three parameter Guggenheim-Anderson-de Boer (GAB) model (Lievense et al., 1992; Rahman, 1995; Timmermann, 2003) as described in Equation 2:

$$Xm = \left[\frac{(CKA_W W_m)}{(1 - KA_W)(1 - KA_W + CKA_W)} \right] \quad (2)$$

*where, W*m implies the water content equivalent to a monolayer coverage. *C* and *K* are constants related to the binding energies and *Aw* corresponds to water activity in the equilibrium.

RESULTS AND DISCUSSIONS

The experimental data obtained through sorption isotherms at 25°C of materials are presented in Table 1 and Table 2 and Figure 1and Figure 2.

After reaching equilibrium state, the water content of the extruded bioplastics showed a tendency (Table 1 and Table 2) to increase as A_W and addition of reinforce material also increased, corroborating with the findings of Chirife and Iglesias, 1978 and Costa et al., 2003.

Table 1. Water content values (Xe) at 25°C of extruded bioplastics added with sunflower cake.

Aw	Sunflower cake content*					
	0.50%	1%	2%	2.50%	5%	10%
0.372	6.1	5.9	6.0	5.9	6.0	6.0
0.462	6.8	6.6	6.4	6.4	6.4	6.8
0.538	9.6	10.3	10.3	10.1	9.9	9.3
0.712	16.4	15.4	15.3	15.1	17.9	22.3
0.788	26.6	25.0	25.3	24.2	24.9	27.1
0.974	35.5	36.0	34.3	35.7	34.8	37.0

Table 2. Water content values (Xe) at 25°C of extruded bioplastics added with castor bean cake.

Aw	Castor cake Content*					
	0.50%	1%	2%	2.50%	5%	10%
0.372	5.8	5.7	5.7	5.7	5.6	5.8
0.462	6.8	7.5	6.8	6.8	6.8	6.6
0.538	9.4	9.4	9.2	9.6	9.3	9.7
0.712	16.6	16.6	16.3	16.8	16.4	16.3
0.788	22.4	22.4	21.8	21.8	22.2	21.8
0.974	36.5	39.6	38.5	36.6	37.9	37.4

The typical sigmoidal curves equilibrium moisture versus relative humidity are shown in Figure 1 and Figure 2. According to BDDT classification (Brunaer et al., 1940) the isotherms curves displayed in Figures 1 and 2 present type II shape. Although both Figures show sigmoid shape curve, the bioplastics added of sunflower cake showed an effect of water sorption as the sunflower content increased, which is contrast to castor bean cake curve. These findings could be attributed to a better association between the castor bean cake, glycerol and the starch matrix which may prevent water sorption.

Up to 58 till 70% RH at 25°C, the bioplastics of cassava flour added of sunflower and castor bean cakes has limited water sorption, which was a relative humidity range of optimal storage condition. After 70% moisture content, the bioplastics present a steeper increase of water content sorption.

According to GAB isothermal modelling (Table 3), experimental values present a good fitting with determination coefficient of 0.99. Similar results were also observed by Lomauro et al. (1985) and Barros Neto et al., (1995). However, bioplastics added with 2 and 5% of sunflower cake presented relative error (e) higher than 5%. By increasing sunflower cake addition the water content monolayer values reduced from 6.51 (1%) to 4.46 (10%). This parameter is particularly important because it indicates the amount of water that is tightly bind, indicating that bioplastic made with 10% is more stable compared to lower levels of sunflower cake content.

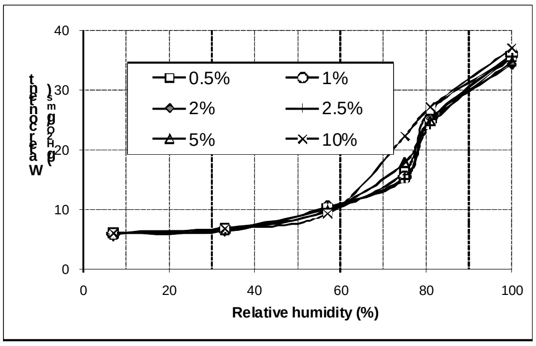

Figure 1. Sorption isotherm curves of water at a temperature of 25C extruder cassava flour bioplastic charged with sunflower cake.

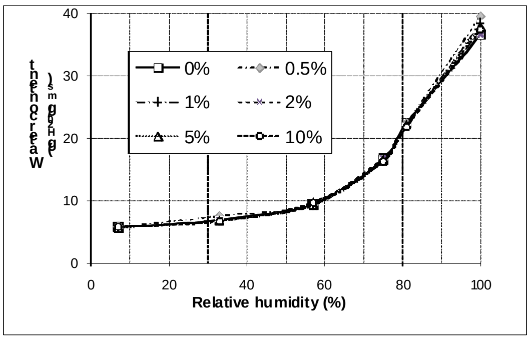

Figure 2. Sorption isotherm curves of water at a temperature of 25°C extruder cassava flour bioplastic charged with castor bean cake.

Table 3. Estimated values obtained from fitting GAB parameters of cassava flour bioplastic added of sunflower reinforce material.

Sunflower (%)	*Xm*	*C*	K	R^2	e
0.50%	5.57	10.8	0.87	0.999	3.55
1%	6.51	13	0.85	0.999	0.78
2%	4.27	18.6	0.92	0.999	5.27
2.50%	4.63	26.5	0.91	1	0.18
5%	4.5	15.5	0.89	0.999	5.35
10%	4.46	14.6	0.95	0.999	0.87

Xm - monolayer water content (g water/g d.s.m.); C and K are constants of GAB model; R^2 - Determination coefficient; e - relative error of Xm parameter.

K values represent the interaction of molecules located at the water multilayer with the adsorbent. The results do not show a clear trend with the addition of sunflower cake at 25°C.

CONCLUSIONS

The experimental data were well adjusted to the GAB isothermal model and showed high determination coefficient. The curves showed a type II shape. Under 0.7 Aw values, the extruded bioplastics did not show reinforce material effect and they are considerably stable. Moreover, the experimental data showed that the extruded cassava flour bioplastics added of micronized oil cakes powder (castor cake and sunflower cake) were less hygroscope than cassava flour. According to GAB isothermal model, the extruded bioplastics (with or without biodiesel coproducts) can be safely stored from up to 70% RH at 25°C.

NOMENCLATURE

Y	amount of water to be added
T	absolute temperature (K)
X_f	final moisture content of the sample
X_i	initial moisture of the sample
C	parameter in the GAB equation
K	parameter in the GAB equation
Pa	Pascal
t	time (s)
A_W	water activity
X	water moisture content (kg-water/kg-dry solid)
W_m	water content equivalent to a monolayer coverage (kg-water/kg-dry solid)
W	weight of sample

ACKNOWLEDGEMENTS

The authors wish to acknowledge and financial support from FAPERJ (E-26/111.483/2008), Embrapa Food Technology and Embrapa Agroenergy and the doctoral scholarship granted to J.A.Ruano-Ortiz (Project Capes-Rede Nanobiotech Brasil n°07).

REFERENCES

Brunauer, S.; Deming, L.S.; Deming, W.S.; Teller, E. On a theory the van der Waals adsorption of gases. Journal of American Chemical Society, v. 62, p. 1723-1732, 1940.

Camire, M. E.; Camire, A.; Krumhar, K. Chemical and nutritional changes in foods during extrusion. Critical Reviews of Food Science and Nutrition, v. 29, n. 1, p. 35-57, 1990.

Chirife, J. y Iglesias, H. A. (1978): “Equations for fitting water sorption iso-therms of food”: Part 1 - a review, J. Food Technol. 13 (3). pp. 159 - 174.

Costa, J. M. C. da; Medeiros, M. F. D. de; Mata, A. L. M. L. da. (2003): “Isotermas de adsorção de pós de beterraba (*Beta vulgaris* L.), abóbora (*Cucurbita moschata*) e cenoura (Daucus carota) obtidos pelo pro-cesso de secagem em leito de jorro: estudo comparativo”, Revista Ciência Agronómica.

Instituto Adolfo Lutz. Normas analíticas do Instituto Adolfo Lutz. 3a edição. São Paulo, 1985, v. 1, 533p.

Lievense, L.C. M.A.M.; Verbeek, T.; Taekema, G.; Meerding and K.Van’t Riet (1992). Modelling the inactivation of *Lactobacillus plantaraum* during a drying process, Chem. Eng. Sci., Vol.47, pp. 87-97.

Muller, C.M.O.; Laurindo, J.B.; Yamashita, F. (2009). Effect of cellulose fibers addition on the mechanical properties and water vapor barrier of starch-based films. Food Hydrocolloids, Vol. 23, n. 5, pp. 1328-1333.

Panadés, G.; Fito, P.; Aguiar, Y.; Villavicencio, M. N.; Acosta, V. (2006). Osmotic dehydration of guava: Influence of operating parameters on process kinetics. Journal of Food Engineering, Vol. 72, pp. 383–389.

Rahman, S. (1995). Food Properties Handbook, CRC press, Boca Raton.

Timmermann, E.O. (2003). Multilayer sorption parameters: BET or GAB values? Colloids and Surfaces A: Physicochem. Eng. Aspects Vol.220, pp. 235-260.