CHARACTERISTICS OF SOME BIOCHEMICAL MATERIALS USED FOR AGRICULTURAL FOIL MULCH

H. M. Mostafa and H. Sourell***

ABSTRACT

A study was conducted at the Institute of Agricultural Technology and Biosystem Engineering, vTI, Germany during the year 2008 to focus on the determination of equilibrium moisture content (EMC) of some bioplastic materials that could be used for agricultural foil mulch. EMC is very important to determine the desirable conditions of microorganism's growth, which causes material deterioration and degradation. Five commercial bioplastic mulches such as Bioflex, Ecoflex, Chitosan, Mater-bi and Bi-OPL were tested at varying temperature (10-50°C) and relative humidity (43-95%). EMC of all materials increased with the increase in relative humidity and decreased with increase in temperature. However, the relative humidity had a greater effect on the change of moisture content than the temperature. The data revealed that Mater-Bi and Chitosan increased EMC by 9.87 and 12.22 percent, respectively by changing the relative humidity from 43 to 95 percent. These changes of relative humidity increased EMC by 1.41, 2.4 and 0.5 percent for Ecoflex, Bioflex and Bi-OPL, respectively.

KEYWORDS: Equilibrium moisture content; mulches; air temperature; relative humidity; Germany.

INTRODUCTION

In the last decade, there has been tremendous interest in bioplastic and biodegradable polymers. There were many attempts to use a bio-filler in thermoplastic polymers because it is a natural polymer, abundantly available and a renewable resource.

With the development of degradable plastics, a group of materials was created with regard to disposal for the first time. Although, the use of degradable plastics is still negligible because of economic reason, yet it has

***Agric. Engineering Department, Agriculture Faculty, Benha University, Egypt, **Institute of Agricultural Technology and Biosystem Engineering, vTI, Germany.**

huge potential being suitable for waste management to close circular flow, saving oil reserves, stabilizing CO_2 emission and offering consumers an environment friendly option.

Biodegradable films can help save energy and are an important issue for environmental protection (13). Molecules of water are constantly leaving and returning to the biomaterial surface. The equilibrium condition exists when the number of molecules of water returns is equal to those leaving the surface. Since the material neither gains nor is loose water considered to have equilibrium moisture content (EMC). When air remains in contact with the material for sufficient time, partial pressure of the water vapor in air reaches equilibrium with partial pressure of the water vapor in material. The moisture content of the material at equilibrium with given environment, i.e. relative humidity and temperature is called the equilibrium moisture content.

There were many attempts to use starch as a bio-filler in thermoplastic polymers. Starch is used as filler because it is a natural polymer, abundant, inexpensive and a renewable resource. Starch is degraded by microorganisms and is suitable for blending with bioplastics and biodegradable polymers. Unfortunately, the mechanical properties of thermoplastic polymer/starch blends are very poor due to the incompatibility and hydrophilic nature of starch (8).

Ashour (6) stated that the equilibrium moisture content of wheat straw increased with increase in relative humidity and decreased with the increase in temperature. He further observed that EMC of barley straw was higher than that of wheat straw. The relative humidity had greater effect on the change of moisture content of bales compared to temperature effect. EMC ranged from 8.4 to 22.9 percent for temperature ranging from 5 to 30°C at 43-96 percent relative humidity.

Paetau *et al.* (11) studied the effect of moisture level in molding material. Soy isolate with four different moisture contents (7.19, 10.0, 12.5 and 16.97%), was molded into plastic specimens at 125^{o}C. At this temperature, complete molding of specimens took place and the tensile strength showed a maximum of 36 MPa at a moisture level of 12.5 percent (Fig. 1). The percent elongation increased as water content increased in the molding material. The moisture content of molding material was crucial for the rigidity and extensibility of the specimens. Moisture contents above 10 percent resulted in more extensible specimens with decreased tensile strength.

Swearing (14) reported that composition of wood and straw are quite similar. Both consist largely of cellulose plus inorganic materials. At about 18 percent moisture content, fungi which are present in wood and straw as spores become active and begin breaking down cellulose, creating what we know as dry rot. Below 18 percent MC, the active fungi go dormant.

Watts *et al.* (16) reported that deterioration of straw can be the result of microbial activity, such as growth, survival, death and toxin production. This activity is a function of environmental variables such as temperature, pH, oxygen, radiation and availability of moisture. Moisture availability for microbial activity is measured by water activity which is numerically equal to the equilibrium relative humidity divided by 100. It is a rule of thumb that below approximately 70 percent equilibrium relative humidity, little microbial activity takes place and the straw is stable. The exact relationship between the equilibrium relative humidity and the moisture content of straw is a function of the type of straw and temperature and is given by the moisture sorption isotherm.

Fully arnorphous bio-plastic applications are limited by the fact that a polymer's Tg (the glass transition temperature) is highly affected by the relative humidity (especially for hydrophilic polymers). Below Tg the material is rigid, and above the Tg it becomes visco-elastic or even liquid. Below this critical threshold, only weak, non-cooperative local vibration and rotation movements are possible. Film relaxation in relation to temperature follows an Arrhenius time course. Above the Tg, threshold, strong, cooperative movements of whole molecules and polymer segments can be observed (7).

Ritschkoff *et al.* (13) studied the mould contamination at 80, 90 or 97 percent RH and 5, 15, 23 and 30°C (at constant humidity and temperature conditions) for several wood-based, stone-based and insulation materials. All building materials tested were susceptible to mould growth at relative humidity higher than 90 percent at temperature above 15°C. However, building materials of different origin showed variable tolerance against fungal growth under the test conditions. In the stone-based materials, the critical humidity level and exposure time required for fungal growth initiation was higher than in the wood-based materials. In the material combinations, initial mould growth principally retarded in the contact surface. Equilibrium moisture content is an important factor in drying and storing the agricultural products, drying and saving building materials such as wood.

Due to lack of information about the thermal, physical and mechanical properties of some bioplastic materials such as foil mulch used in agriculture, this research was initiated. The main aims were (i) to obtain the EMC of bioplastic materials, (ii) to identify the properties of these materials and (iii) to explore the possibility of using as biodegradable tubes for micro-irrigation.

MATERIALS AND METHODS

This study was conducted at the Institute of Agricultural Technology and Biosystem Engineering, vTI, Germany during the year 2008. The equilibrium moisture contents were determined for five commercial bioplastic samples (Bioflex, Ecoflex, Mater Bi, Chitosan and Bi-OPL) used as agricultural mulch film according to DIN EN ISO 12571 (1996).

Ecoflex® F BX 7011 is a biodegradable aliphatic-aromatic copolyester based on the monomers 1, 4-butanediol, adipic acid and terephthalic acid for film extrusion. It has been developed for the conversion to flexible films using a blown film or cast film process. Typical applications are packaging films, agricultural films and compost bags (5).

Bio-Flex® film compounds are innovative PLA/copolyester blends. The excellent processing qualities stem from outstanding compatibility of the polymeric components polylactic acid (PLA) and the biodegradable copolyester. Bio-Flex ® film compounds do not contain starch or its derivatives (4).

Chitin, a polysaccharide of animal origin, is obtained from seafood industrial waste. It occurs in the skeletal material of crustaceans such as crabs, lobsters, shrimps, prawns and crayfish. Chitosan is the deacetylated product formed by treatment of chitin with concentrated (50%) caustic alkali. Thus Chitosan is safe (nontoxic), biocompatible and biodegradable (12, 17).

Mater-Bi® is a biodegradable thermoplastic material made of natural components (corn starch and vegetable oil derivatives) and of biodegradable synthetic polyesters. The material is certified as biodegradable and compostable in accordance with European Norm EN 13432 and with the national regulations UNI 10785 and DIN 54900 (2).

Bi-OPL is biodegradable film mulching produced from poly lactic acid (PLA) which is made of degradable materials (corn) and compostable in accordance with DIN EN13432 (3).

Samples of 10 x 10 cm were taken and put on a wire mesh above a plastic dish containing a saturated salt solution. The samples, wire mesh and dishes were placed inside a basket. The basket was placed in a plastic bag with an air-tight seal. These bags were placed inside a climate chamber (3.5 m x 2.75 m x 3.0 m) at different temperatures (10, 20, 30, 40, and 50 °C) and relative humidity values (43, 53, 65, 75, 85, and 95 %).The development was controlled with combined T/RH sensors until a constant relative humidity inside the bag was reached. After two weeks, samples were weighed and the moisture contents were calculated.

Capacitive humidity sensors (Aluminum 12 mm $\phi \pm 2$ % for RH, and 1 K for temperature accuracy, made in Germany) contained a glass substrate with a humidity-sensitive polymer layer between two metal electrodes. The capacity of thin-film capacitor changed with the absorption of water depending on relative humidity.The measuring signal is directly proportional to the relative humidity and is not dependent on the atmospheric pressure.

In order to obtain different relative humidity values in the surrounding materials, the chemical substances were used as listed in Table 1.

Moisture content for the materials was measured according to ASHRAE (1). The materials were put in the drier at constant weight. The following equation was used to calculate the MC:

$$MC\ (\%) = \frac{(W_m - W_d)}{W_d} * 100$$

Where:

MC : Moisture content (%, db)
W_m : Moist weight = (kg)
W_d : Dry weight = (kg)

Table 1. Chemical substances used for adjusting different relative humidity values.

Name	Materials	Relative humidity (%)
Sodium sulfate	$Na_2SO_4.10\ H_2O$	95
Potassium chloride	KCl	85
Sodium chloride	NaCl	75
Sodium nitrite	$NaNO_2$	65
Magnesium nitrate	$(Mg\ NO_3).6\ H_2O$	53
Potassium carbonate	$K_2CO_3.2\ H_2O$	43

RESULTS AND DISCUSSION

Mater-Bi

The results (Table 2, Fig. 1) revealed that the equilibrium moisture content of Mater-Bi increased with the increase in relative humidity and it decreased with increase in temperature. It seems that relative humidity had a greater effect on the equilibrium moisture content than temperature, where changing the relative humidity from 43 to 95 percent increased moisture contents of the material by 12.17 percent at 10°C temperature. On the other hand, increasing the temperature from 10 to 50°C decreased the equilibrium moisture content of the material by 4.3 percent at 43 percent relative humidity. Increasing the relative humidity from 43 to 95 percent at 50°C increased the moisture content by 9.41 percent. The moisture contents were reduced by 7.06 percent with the increase in temperature from 10 to 50°C at 95 percent relative humidity.

Table 2. Equilibrium moisture content (% db) of Mater-Bi.

RH%	Temperature°C					Average
	10	20	30	40	50	
43	4.30	4.30	2.15	1.08	0.00	2.37
53	6.38	6.38	6.38	5.32	4.26	5.74
65	6.38	6.38	6.38	5.32	4.26	5.74
75	6.38	6.38	6.38	5.32	4.26	5.74
85	8.70	8.70	8.70	7.61	6.52	8.04
95	16.47	12.94	11.76	10.59	9.41	12.24
Average	8.10	7.51	6.96	5.87	4.78	6.65

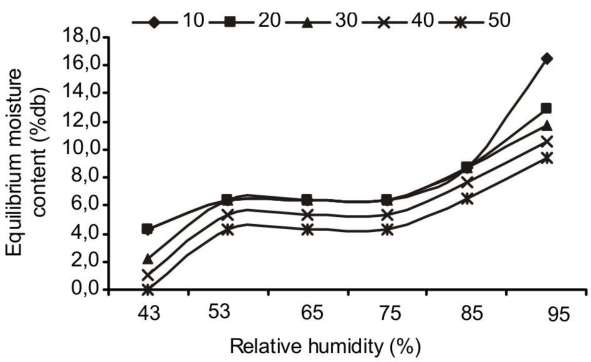

Fig 1 Equilibrium moisture content of Mater Bi

The average of EMC at 43 to 95 percent relative humidity ranged from 2.37 to 12.24 percent, on the other hand it ranged from 8.10 to 4.78 percent for 10 to 50°C (Table 2).

At low relative humidity (43 %) maximum EMC was 4.30 percent at 10°C and zero at 50°C. As relative humidity rises, the EMC also rose to 16.47 percent at 10°C and 9.41 percent at 50 °C.

Ecoflex

The results (Table 3, Fig. 2) show that at low relative humidity (43 %), maximum EMC was 5.88 percent at 10°C while it was low (3.53%) at 50°C. With the increase in relative humidity, EMC rose to 8.24 percent at 10°C and 7.06 percent at 50°C. It is also noticed that change in relative humidity from 43 to 95 percent led to an increase of 2.36 percent in the moisture content of material at 10°C temperature. On the other hand, increasing the temperature from 10 to 50°C caused a decrease of 2.35 percent EMC of Ecoflex at 43%) RH. Higher temperature (50°C) and relative humidity (43 to 95 percent) caused an increase of 3.53 percent in EMC. This increase was 1.18 percent when the temperature increased from 10 to 50 °C at 95 percent relative humidity.

Table 3. Equilibrium moisture content (% db) of Ecoflex.

RH%	Temperature °C					Average
	10	20	30	40	50	
43	5,88	5,88	5,88	4,71	3,53	5,18
53	5,88	5,88	5,88	4,71	3,53	5,18
65	5,88	5,88	5,88	5,88	4,71	5,65
75	5,88	5,88	5,88	5,88	5,88	5,88
85	7,06	7,06	7,06	5,88	5,88	6,59
95	8,24	8,24	8,24	7,06	7,06	7,76
Average	6,47	6,47	6,47	5,69	5,10	6,04

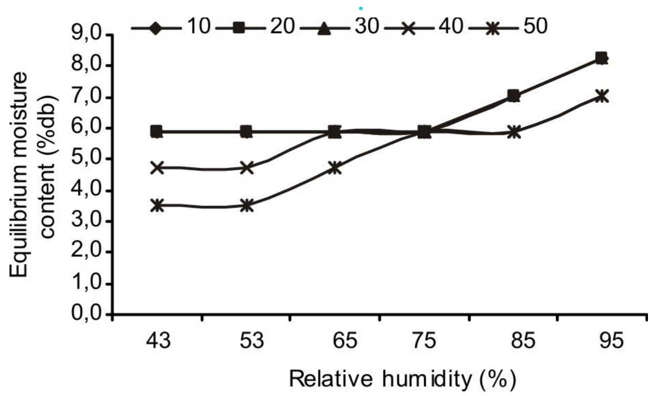

Fig. 2 Equilibrium moisture content of Ecoflex

Chitosan

Maximum equilibrium moisture content for Chitosan materials at low relative humidity (43 %) was 7.64 percent at 10°C while it was low (3.47%) at 50°C (Table 4, Fig. 3). As relative humidity increases, the EMC reached to 19.44 percent at 10°C and 13.19 percent at 50°C. It is also noticed that changing the relative humidity from 43 to 95 percent leads to an increase of 11.80 percent in moisture content of the material at 10°C. On the other hand, increasing the temperature from 10 to 50°C caused a decrease of 4.17 percent in EMC of Chitosan. At higher temperature (50°C) and relative humidity (95%), EMC increased by 9.72 percent. This increase was 6.25 percent when the temperature increased from 10 to 50°C at 95 percent relative humidity.

Table 4. Equilibrium moisture content (% db) of Chitosan.

RH (%)	Temperature °C					Average
	10	20	30	40	50	
43	7,64	6,94	4,17	3,47	3,47	5,14
53	11,54	11,54	7,69	6,15	5,38	8,46
65	12,32	12,32	11,59	11,59	10,14	11,59
75	11,54	15,38	15,38	11,54	11,54	13,08
85	17,04	18,52	18,52	13,33	12,59	16,00
95	19,44	22,92	18,06	13,19	13,19	17,36
Average	13,25	14,60	12,57	9,88	9,39	11,94

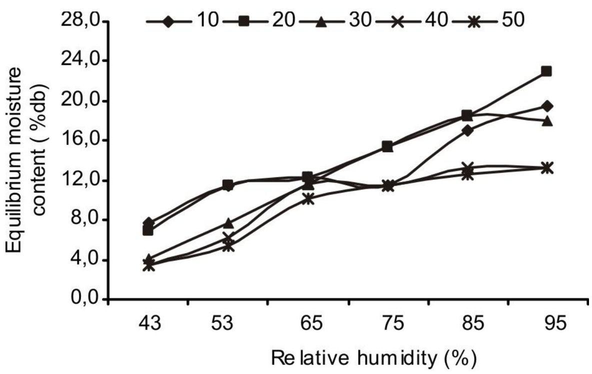

Fig. 3 Equilibrium moisture content of Chitosan

Bioflex

Bioflex also followed the same trend as by Ecoflex and Mater-Bi. The EMC increased with increase in relative humidity. It decreased at small rate with the increase in temperature (Table 5, Fig. 4). The results revealed that Bioflex at 10, 20, 30 and 40°C increased the moisture content by 2.37 percent when relative humidity increased from 43 to 95 percent. However, increasing the temperature to 50°C resulted in a small decrease of 0.2, 0.21, 0.14, 0.31, 0.3 and 0.08 percent in EMC at relative humidity of 43, 53, 65, 75, 85 and 95 percent, respectively.

Table 5. Equilibrium moisture content (% db) of Bioflex.

RH (%)	Temperature °C					Average
	10	20	30	40	50	
43	1.89	1.89	1.88	1.85	1.69	1.84
53	1.96	1.96	1.96	1.90	1.75	1.91
65	2.08	2.08	2.08	2.08	1.94	2.05
75	2.42	2.42	2.42	2.42	2.11	2.36
85	3.35	3.35	3.35	3.35	3.05	3.29
95	4.26	4.26	4.26	4.26	4.18	4.24
Average	2.66	2.66	2.66	2.64	2.45	2.62

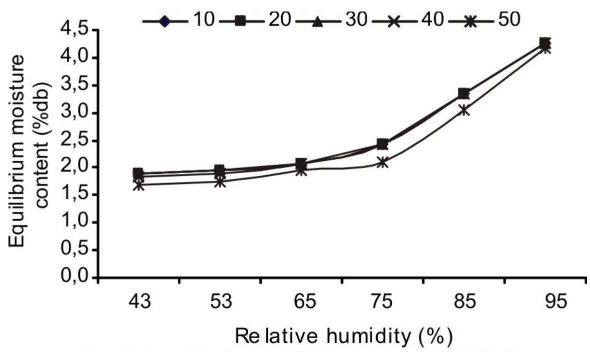

Fig. 4 Equilibrium moisture content of Bioflex

Bi-OPL

The results (Table 6, Fig. 5) indicated that Bi-OPL performed similar to Bioflex. By changing the relative humidity from 43 to 75 percent and temperature from 10 to 50°C, the EMC was comparatively stable (1.03%). On the other hand, mean of EMC increased to 0.12 and 0.5 percent when relative humidity increased to 85 and 95 percent, respectively. This shows that neither the temperature (10 to 50°C) nor the relative humidity (43 to 95%) had any significant effect on EMC of Bi-OPL.

Table 6. Equilibrium moisture content (% db) of Bi-OPL.

RH (%)	Temperature °C					Average
	10	20	30	40	50	
43	1.03	1.03	1.03	1.03	1.03	1.03
53	1.03	1.03	1.03	1.03	1.03	1.03
65	1.03	1.03	1.03	1.03	1.03	1.03
75	1.03	1.03	1.03	1.03	1.03	1.03
85	1.24	1.24	1.24	1.03	1.03	1.15
95	1.65	1.65	1.65	1.44	1.24	1.53
Average	1.17	1.17	1.17	1.10	1.07	1.13

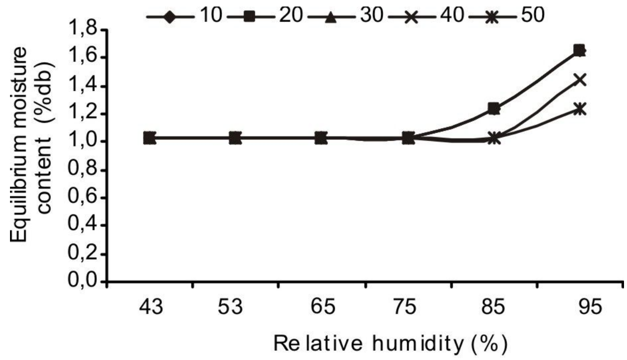

Fig. 5 Equilibrium moisture content of Bi-OPL

The results showed that both for Mater-Bi and Chitosan, the EMC increased by 9.87 and 12.22 percent, respectively when the relative humidity increased from 43 to 95 percent. However, there is negligible effect on EMC by changing the relative humidity from 43 to 95 percent for Ecoflex (1.41%), Bioflex (2.4%) and Bi-OPL (0.5%). This may be due to the fact that moisture content is identical to the sorption isotherms, where water is adsorbed from the vapor of ambient air, and the moisture content is in equilibrium with the ambient relative humidity. Two mechanisms are responsible for this sorption phenomenon, at low relative humidity values. Water molecules are attached to the pore film wall forming a thin water film, as relative humidity increases. The film becomes thicker and capillary condensation takes place in the narrow pores. Although these two mechanisms overlap but at high relative humidity, the capillary condensation is more dominant.

Equilibrium moisture content of bioplastic materials increased with the increase in relative humidity at same temperature. That was due to the vapor pressure deficit (VPD) decreases with increasing relative humidity which creates an atmosphere close to saturation. This increases the ability of sheet thickness to absorb more moisture from the surrounding atmosphere. On the other hand, with increasing temperature from 10 to 50 °C, equilibrium moisture content decreases according to Krus (9*)* and Künzel (10)*.*

CONCLUSION

The results of this study conclude that the equilibrium moisture content of all materials studied increased with increasing relative humidity and decreased with increasing the temperature. The equilibrium moisture contents of Chitosan and Mater-Bi were higher than Ecoflex and Bioflex. The EMC was the lowest for Bi-OPL. As it is well known that temperature and relative humidity play an important role in the microorganism activity which can attach and degrade the bio materials, so each of Ecoflex, Bioflex and Bi-OPL, may hold for a longer period of time than Chitosan and Mater-Bi as a mulch film. However, the effect of soil type and length of time required for the degradation of these materials must be studied.

REFERENCES

1. Anon. 1997. ASHRAE Handbook, Fundamentals. New York. American Society of Heating and Refrigerating and Air Conditioning Engineers, Inc.
2. Anon. 2008. http://www.materbi.com/ing/html/PDF/EPD_PE_180202.pdf. Novamont company.
3. Anon. 2008. www.oerlemansplastics.nl and www.azenos.com_nav-info_biopl_php. Oerlemansplastics company.
4. Anon. 2008. Production description. FKUR Company. (http://www.fkur.de/?page=95).
5. Anon. 2007. Production information, Ecoflex® BASF Company, Brochure (www.basf-ag/ecoflex)
6. Ashour,T.H. 2003. The Use of Renewable Agricultural By-products as Building Materials. Ph.D Thesis, Benha University, Egypt. (http://www.downloads.fasba.de/TahaAshour-2003-complete.pdf).
7. Cuilbert S., and N. Contard. 2005. Innovations in Food Packaging: Agro-polymers for edible and biodegradable films: review of agricultural polymeric materials, physical and mechanical characteristics. Elsevier Ltd.
8. Kaewta, K. and V. Tanrattanakul. 2008. Preparation of cassava starch grafted with polystyrene by suspension polymerization. Carbohydrate Polymers in press.

9. Krus, M. 1995. Moisture Transport and Storage Coefficients of Porous Mineral Building Materials. Theoretical Principles and New Test Methods. Disseration. Fraunhofer Institute for Building Physics, University of Stuttgart, Germany.
10. Kuenzel, H. 1991. Simultaneous Heat and Moisture Transport in Building Components. One and two-dimensional Calculation Using Simple Parameters. Dissertation. Fraunhofer Institute for Building Physics, University of Stuttgart. Germany.
11. Paetau, I., C. Chen and J. Jane. 1994. Biodegradable Plastic Made from Soybean Products. 1. Effect of Preparation and Processing on Mechanical Properties and Water Absorption. Ind. Eng. Chem. Res. Vol. 33(7).
12. Radhakumary, C., Prabha D. Nair1, Suresh Mathew and C.P. Reghunadhan Nair. 2005. Biopolymer Composite of Chitosan and Methyl Methacrylate for Medical Applications. Trends Biomater. Artif. Organs. Vol. 18 (2):
13. Ritschkoff, A., Viitanen and Koskel. 2000. The response of building materials to the mould exposure at different humidity and temperature conditions. Proceedings of Healthy Buildings. Vol. 3: 317-322.
14. Swearing, J. 2001. Moisture barriers in straw-bale construction. www.skillful-means.com
15. Tien, C. Le., M. Letendre, P. Ispas-Szabo, M. A. Mateescu, G. Delmas-Patterson, H.L. Yu and M. Lacroix, 2000. Development of biodegradable films from whey proteins by cross-linking and entrapment in cellulose. J. Agric. Food Chem., 5566-5575 Vol. 48
16. Watts, K.C, K. I. Wilkie, K. Tompson and J. Corson. 1995. Thermal and mechanical properties of straw bales as they relate to a straw house. Canadian Society of Agricultural Engineering, Paper No. 209.
17. Yadav, A. V. and S. B. Bhise, 2004. Chitosan: A potential biomaterial effective against typhoid. Current Science. Vol. 87(9).