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Note

Coating of fertilizers by degradable polymers

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Abstract

The conventional agriculture leads to some important pollution of ground water (particularly, by nitrates). The solution is the coating of fertilizers by degradable polymers. In this work, we have

- studied the water vapour and liquid diffusion through polymer films detached from their support. Therefore, we may classify polymers as a function of their properties like water vapour and liquid barrier. We may choose the best polymer(s) for coating.
- coated fertilizers by chosen polymer(s) with mechanical techniques such as fluidised bed and pan coating. Moreover, the electron microscopy used to see the quality of the wall has showed the presence of pores due to the rapid evaporation of solvent. A drying in air current and an annealing could be done to avoid this problem.
- followed the ions release of fertilizers immersed in distilled water by conductimetry. The more interesting result was obtained with fertilizers coated by polylactic acid. In effect, the total release reached three weeks.

Keywords: Coating pan; Encapsulation; Fertilizer; Fluidised bed; Polylactic acid; Permeability

The use of huge quantity of fertilizers with the conventional agriculture leads to some important environmental problems. One of these problems is the overconsumption of fertilizers to fight against the natural leaching leading to a loss of around 2/3 and causes the pollution of ground water by nitrates in addition to others sources of pollution (pesticides…). One solution of this problem is the encapsulation of fertilizers by membranes to control the diffusion of water and the release of the water-soluble active agent. Moreover, the use of degradable polymers avoiding additional residue in the soil will increase ecological effects of this procedure. Others similar systems have already been used in the horticultural domain (fertilizers Osmocote® (Lamble and Hubertus, 1986) for rose trees marketed by FERTILIGENE Society), but their cost is higher for cultivation on a large scale. The principal encountered difficulty is the choice of the right coat polymer. Water vapour permeability may aid in this choice.

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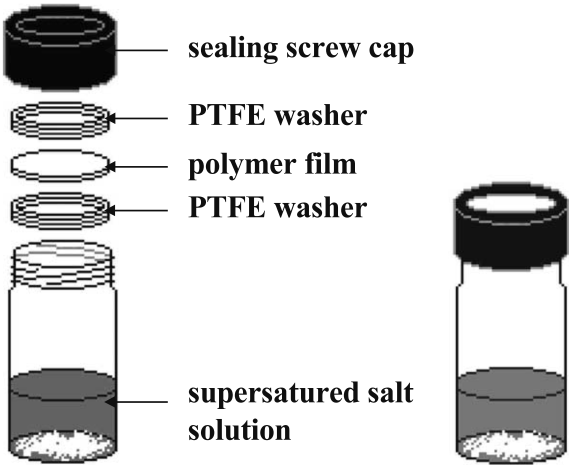

Fig. 1. Cell.

Water vapour permeability was determined through polymer films detached on their support. Polymer films were prepared by dissolving in an organic volatile solvent (dichloromethane). The solution is also deposited on a flat metal plate and is levelled with a knife to ensure uniform thickness. The film drying is made by evaporating organic solvent. This step is realised in a closed box in Plexiglas to maintain a saturated atmosphere and further a slow film drying. The dry film is detached from the plate.

Membrane circles of uniform size were punching from these films and their thickness was measured with the help of a thickness gauge. The membranes were sealing with the aid of rubber and teflon washers over shallow cups containing a supersaturated solution of ammonium chloride (vapour pressure around 18.6 mmHg at 25 °C). Then, these sealed cups were placed inside a desiccator containing phosphorus pentoxide (P_2O_5), ensuring zero water vapour pressure.

(Fig. 1) Cells were weight every day and the cumulative weight loss was plotted as a function of time (Fig. 2). Whereas the stationary regime was reached, permeability coefficient was determined by the slope by using Eq. (1).

$$\frac{\Delta m}{\Delta t} = K\frac{A\,\Delta p}{l} \qquad (1)$$

with Δm, weight loss (mg); Δt, time (s); l, average thickness (cm); A, area (cm^2); Δp, pressure difference (Pa); K, permeability coefficient (cm^2 s^{-1} Pa^{-1}).

The physico-chemical properties of polymer are listed in Table 1. The permeability coefficients K are calculated with the linear portion of the slope, indicating that the stationary regime was reached.

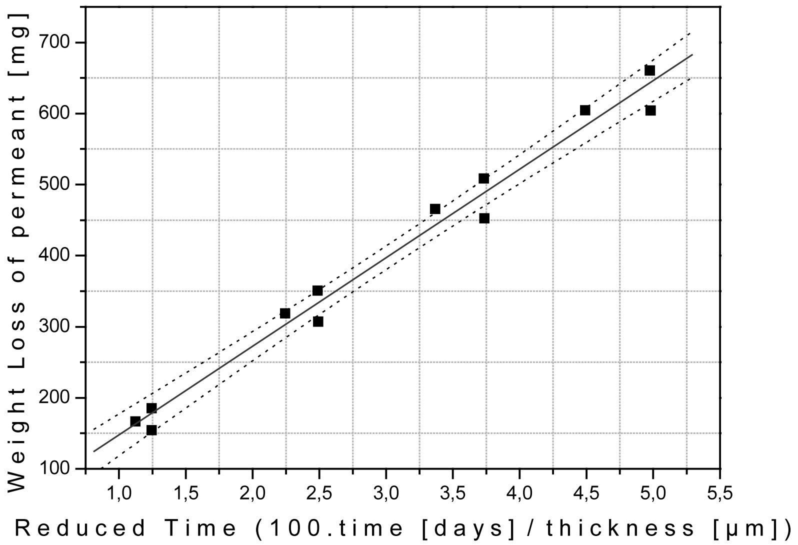

Fig. 2. Example of plot (cumulative weight loss vs reduced time) on modified starch films.

Table 1
Physico-chemical and water vapour permeability of studied polymers

Trade name	Name	M_w	I_p	T_g (°C)	T_f (°C)	K × 10^{13} (25 °C) ($cm^2 s^{-1} Pa^{-1}$)	Manufacturer
Parafilm	Polyethylene	1117 000	1.5	–	–	77	American National Can
Biopol 300G	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (94/6)	565 600	2	4	169	190 ± 80	ICI
Biopol 400G	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (90/10)	350 900	2	6	160	250 ± 50	ICI
Biopol 600G	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (88/12)	374 000	2.1	−1	157	300 ± 50	ICI
LPLA	Poly-L-lactic acid	76 000	1.7	60	180	1950 ± 470	Fluka
PLA50A	Poly-D,L-lactic acid (50/50)	34 000	2.1	60	-	1700 ± 80	Phusis
PLA50B	Poly-D,L-lactic acid (50/50)	70 000	1.6	60	-	1700 ± 150	Phusis
PLA52	Poly-D,L-lactic acid -(52/48)	122 500	2.5	50	-	1650 ± 210	Galactic
PET	Biodegradable polyterephtalate	46 000	1.5	−37	109	3150 ± 100	Eastman
PCL	Poly-ε-caprolactone	109 000	1.8	−59	59	5200 ± 500	Aldrich
PHO	Poly (3-hydroxyoctanoate)	214 000	1.4	−33	53	2200 ± 240	Pasteur
Starch	Modified starch amylose/amylopectin (80/20)	–	–	–	105	9950 ± 780	Roquette Frères

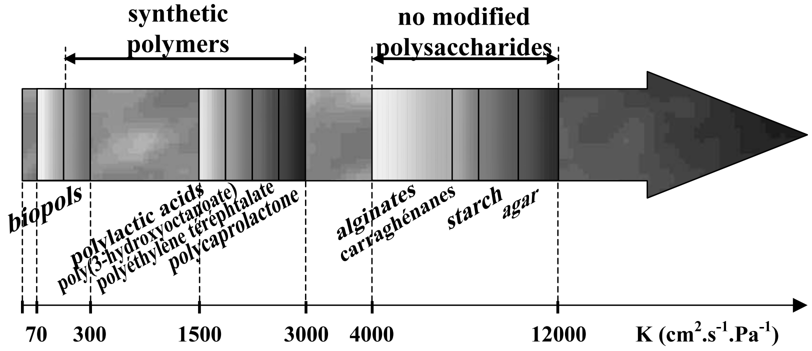

Fig. 3. Classification of polymers.

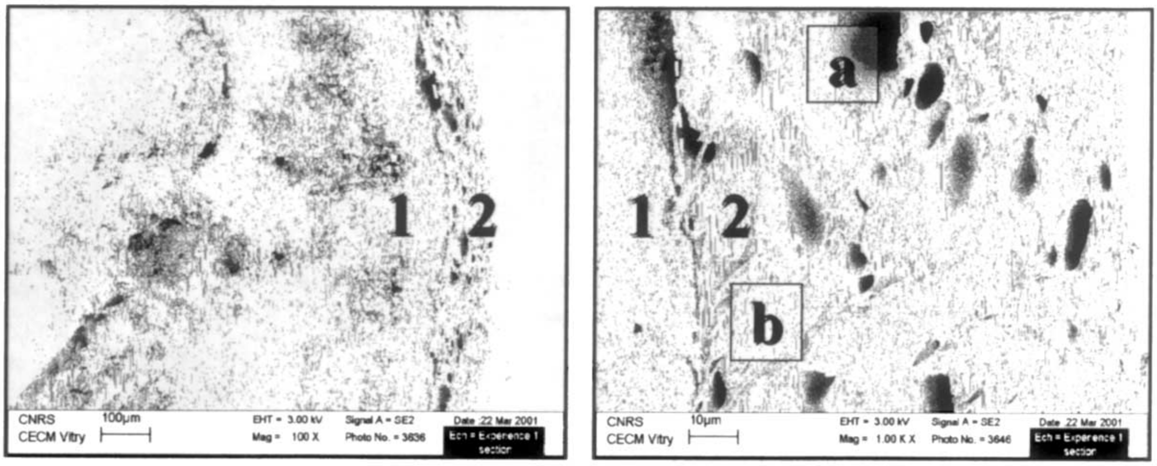

Fig. 4. Granule section coated by polylactic acid in fluidised bed.

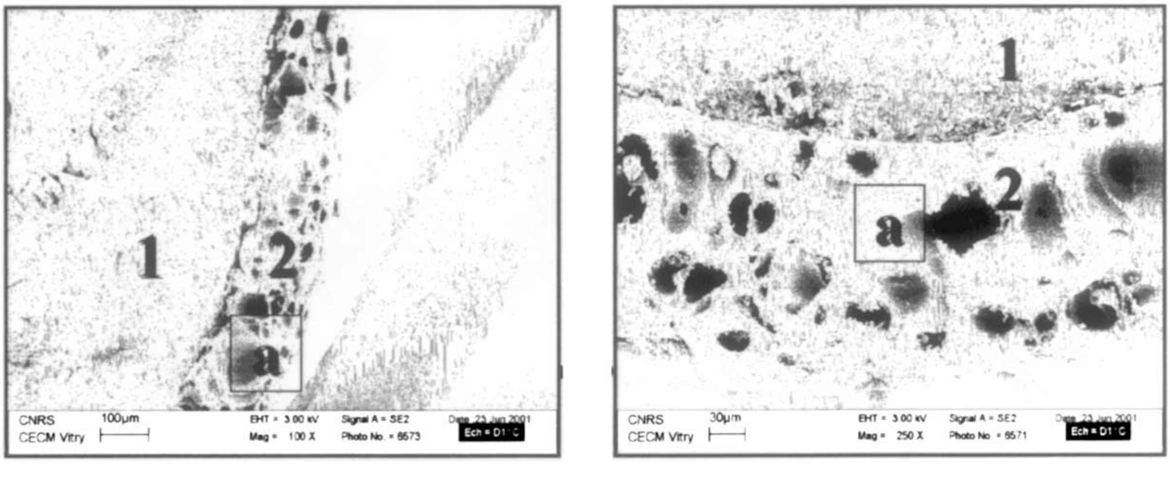

Fig. 5. Granule section coated by polylactic acid in coating pan.

It is obtained using the Eq. (1). The values for permeability of different studied polymers are also listed in Table 1 and are given in conventional unity i.e. in cm^3 (STP)cm cm^{-2} s^{-1} Pa^{-1} at 25 °C.

The results of permeability coefficient (Table 1) show that the different Biopols have the lowest permeability coefficient among all studied (bio)degradable polymers. It is probably relied on the high cristallinity of polymers. In effect, in semicrystalline polymers, the solubility occurs exclusively in the noncrystalline regions and is proportional to the amorphous content. Moreover, cristallinity affects the diffusion too. Crystallites interrupt the flow lines, leading to increased tortuosity of the diffusion path. They can also act as a crosslink, restraining the mobility of the chains. Therefore, polymers cristallinity tends to reduce the water vapour permeability (Barrie, 1968; Mark and Gaylord, 1968). The optical activity of PLA (Siparsky et al., 1997) does not seem to influence the circulation of water vapour through

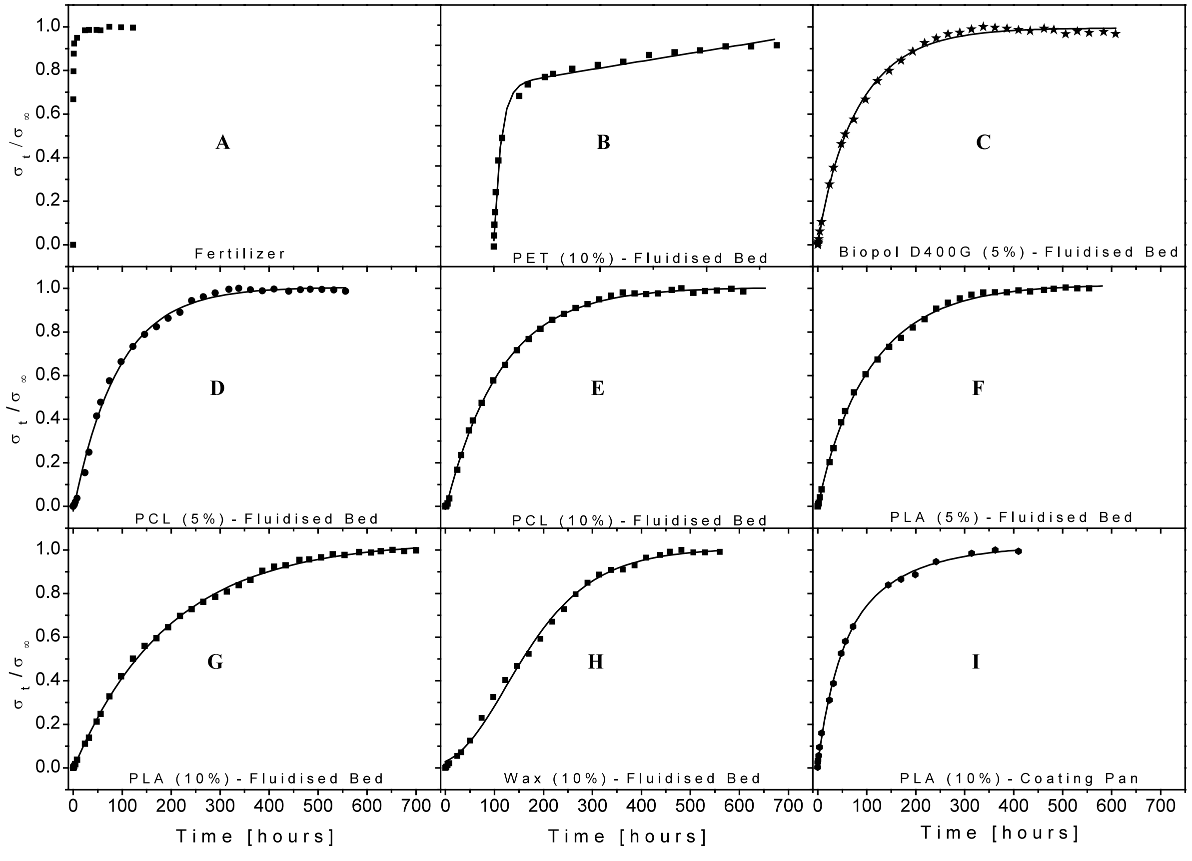

Fig. 6. Plots of ions release (conductivity vs time).

Table 2
Determination of kinetic coefficients

	A	B	C	D	E	F	G	H	I
$t_{\frac{1}{2}}$ (h)	0.2	6.5	56	66	83	73	122	158	45
t_{∞} (h)	74	242	462	433	482	482	628	531	362

the membrane. Although PHO and PCL have a more hydrophobic structure, their permeability coefficients are higher than PLA. This observation is probably relied on the low glass transition temperature (PHO: -33 °C and PCL: -60 °C). The mobility of chains makes easier the water molecules circulation through the film. Moreover, the presence of bulky group in the case of PHO (C_5H_{11}) leads to a gap between macromolecular chains, making an easier diffusion of the water molecules. This behaviour was already observed (Morgan, 1953) with polymethacrylates. In effect, the water permeability coefficients were respectively of 2850, 3900, 4430 $cm^2\,s^{-1}\,Pa^{-1}$ with a methyl, an ethyl and a butyl bulky group. Polymers with hydroxyls groups have high permeability coefficient probably due to the most affinity for water molecules.

Polymers classification (Fig. 3) as a function of water vapour permeability coefficient allows to differentiate two types of polymers:

- synthetic polymers, with a small permeability coefficient ($K \leqslant 3000$ $cm^2\,s^{-1}\,Pa^{-1}$) due to a more hydrophobic structure,
- no modified polysaccharides, with a higher permeability coefficient ($K \geqslant 4000$ $cm^2\,s^{-1}\,Pa^{-1}$) due to hydrophilic groups (hydroxyls).

The permeability results show that the best polymers for coating are Biopols and polylactic acid. But we have chosen polylactic acid because Biopols are very crystalline (low solubility).

We have used two industrial coating techniques to encapsulate fertilizer granules:

- HUTTLIN fluidised bed (KUGEL-COATER®). HUTTLIN fluidised bed is a Turbojet system with a lamellae base.
- SCHINDLER coating pan

This is a classical coating pan and the polymer solution was sprayed with an airgun.

After coating, the quality of polymer wall was carried out by Scanning Electron Microscopy (S.E.M.). Photos (Fig. 4 and Fig. 5) show a spongiest wall structure by coating pan (Fig. 5). The number and the size of pores are more important. It is probably due to the drying, which is more difficult to control with this coating technique. A drying in air current and an annealing could be done, to avoid this problem.

The release of fertilizer ions was followed by conductimetry. Twenty gram of coated fertilizer were immersed in 300 ml of deionised water. A conductivity cell is placed and the solution conductivity is measured every day (Fig. 6).

An exponential equation ($y = A_1(1-\exp(-x/t_1)+A_2(1-\exp(-x/t_2))$) was used to fit the experimental data and to determine (by extrapolation) the times necessary to reach respectively 50% of release ($t_{\frac{1}{2}}$) and the asymptote (t_∞). These times are presented in Table 2.

Comparing the different times ($t_{\frac{1}{2}}$), we can conclude that the best technique is to coat by fluidised bed with polylactic acid ($t_{\frac{1}{2}} = 122$ h). The total release is reached in about 26 days. The fertlilzer granules coated with the same polymer, using the coating pan present a quicker release ($t_{\frac{1}{2}} = 45$ h). These results confirm the different coating quality observed by S.E.M.

References

Barrie, J.A., 1968. Water in polymers. In: Crank, J., Park, G.S. (Eds.), Diffusion in Polymers. Academic Press, London and New York, pp. 281–282.

Lamble, Hubertus, J.-M., 1986, Granular Fertilizer Composition having Controlled Release and Process for the Preparation Thereof, European Patent 0184869 A1, 18 June.

Mark, H.F., Gaylord, N.G., 1968. Permeability. Encyclopedia of Polymer Science and Technology 9, 794–795.

Morgan, P.W., 1953. Structure and moisture permeability of filma-forming polymers. Ind. Eng. Chem. 45, 2296–2306.

Siparsky, G.L., Voorhees, K.J., Dorgan, J.R., Schilling, K., 1997. Water Transport in Polylactic Acid (PLA), PLA/Polycaprolactone Copolymers, and PLA/Polyethylene Glycol Blends. J. Env. Pol. Deg. 5 (3), 125–136.