APPLICATION OF RADIATION TECHNOLOGY TO BIOMASS CONVERSION PROCESSES

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ABSTRACT

This paper reports the work done at the Instituto de Pesquisas Energéticas e Nucleares - IPEN, in the following research projects:

1) wood powdering of pre-irradiated chips;
2) effect of combining electron beam processing (EBP) with other pretreatments on the saccharification of lignocellulosic materials (*);
3) radiation immobilization of enzymes (*).

The EBP of eucalyptus chips at an average dose of 1.5 x 10^5Gy allowed a reduction of the energy required to produce a given weight of wood particles smaller than 300µm by a factor of five. Wood powder of this particle size proved to be an excellent fuel for suspension firing system and could be used as raw material to feed continuous hydrolytic processes.

Conversion efficiencies of 25.8% and 53.4%, respectively, were obtained in the production of reducing sugar by enzymatic hydrolysis of eucalyptus wood and sugarcane bagasse when that materials were previously irradiated at 10^5Gy, pulverized at 50 Mesh and impregnated with 2% NaOH solution.

Imobilization of cellulase by radiation induced polymerization of hydroxi-ethyl-methacrylate (HEMA) was effective when made at -78°C in the presence of silica gel adsorbents or polyethylene glycol.

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1.0.0 INTRODUCTION

Three potential applications of radiation technology in the field of biomass conversion are being presently investigated at IPEN-CNEN facilities. They are:

1) electron beam processing (EBP) of wood chips to improve grinding efficiency in the production of fine wood powder;
2) combination of EBP with other physical and chemical pretreatments for enhancing cellulose saccharification of ligno-cellulosic materials.
3) immobilization of enzyme in plastic composites by radiation induced polymerization at low temperatures.

The relevant features of these techniques will be breafily discussed in the following sections.

2.0.0 WOOD POWDERING OF PRE-IRRADIATED CHIPS

Wood can be either burned directly as a fuel in steam boilers and any kind of thermal installations, or used as a raw material for continuous hydrolytic processes.

In the case of direct combustion, wood and other ligno-cellulosic materials can be burned under different initial conditions of aggregation, consistence and moisture content which, in turn, define not only the possibilities to apply such a products in an specific process but, also, the economy eventually expected from their use as fuel.

No matter the type of thermal process that may be considered it will be necessary, in order to guarantee its efficiency and continuity,to keep a minimum of uniformity in the fuel physical and chemical characteristics and to assure its regular supply on long term basis.

If, in a process already established, the substitution of fluel oil by wood derivative products is possible, the following alternative will appear:

1) to modify substancially the installation in order to allow the use of primary wood products (logs, chips and wastes from different origins), even at the expenses of a significant loss in the overall thermal efficiency of the system;
2) to process the wood in such a way that the final product (gas, ethanol or wood flour) can be used with minimum modifications in the existing installation and maximum benefit of its heat power.

The first option, probably because it requires a technology more accessible than the second, and also lower investiments, has been up to now, preferentialy accepted by industry.

There are, nevertheless, a great deal of thermal units,particularly kilns and calcinations furnaces used in cement and ceramic industries , (that are responsible for an important part of the fuel oil consumed in the country) in which, because of technical reasons, the first option is not feasible or it can attend only a fraction of the process heat power demand.

It is in such industries, in those that did not adopt yet alternative energy solutions and in the new thermal facilities to be installed, where the other wood derivative fuels obtained by advanced transformation processes, are potentialy usable in large scale. For this to be practicable, the higher costs of the pretreated wood, prior its use as fuel , should be compensated by the resultant benefits (1). These prospects are specially valid since certain processes that were previously considered anti-economical or unpracticable in industrial scale, may become feasible on account of the development of new technologies in the wood conversion methods.

Pulverization of wood represents and advanced stage in the conversion of a primary fuel (logs) into another of superior quality from different aspects, namely:

a) the storage, feeding and burning systems can be standardized for automatic and reliable operation, not requiring any modification in the existing installation except the change of burners (2);

b) the combustion can be started and stopped instantaneously and the heat generation adjusted to attend the steam or heat demand without delay;

c) because of its fast combustion, the heat power per unit of mass (kcal $kg^{-1}s^{-1}$) released by pulverized wood is greater than for logs, chips, pellets or gross particles, that require longer time to reach the ignition temperature; this, added to the fact that the combustion takes place with a minimum excess of air, allows higher flame temperature for specific applications;

d) the wood flour can replace fuel oil and powdered coal in kilns or calcination furnaces without air pollution problems.

In the U.S.A. many large industrial-sized coal-fired boilers are being designed with wood waste firing capability and it was observed that design work is moving forward in the development of a pulverized log fuel firing systems using powdered coal burners (3). Such burners generally require a fuel that is dried to a maximum of 12% moisture and pulverized to a 50 mesh size.

Under natural conditions the reduction of wood and correlate products to such a fine dried particles demands a rather high energy consumption and may cause excessive wear of the particular mill employed.

Studies developed by the IPEN and complemented with experimental tests at a semi-industrial mill installation showed that previous irradiation of eucalyptus and pine wood with high energy electrons at doses of about 10^5Gy (10Mrad), greatly increases the pulverization efficiency of grinding processes. Similar results were obtained by M.Kamamura et al

(4) for the pretreatment of lignocellulosic wastes.

The interaction between high energy electrons and wood constituents cause the breakage of lignocellulosic macromolecules (i.e. depolymerization) and for radiation doses above 10^5Gy this effect is traduced in a significant loss of fiber physical integrity.

As a result, wood is converted into a friable product, easy to be pulverized by the mechanical action of a hammer mill.

This effect of radiation on wood grinding, was quantitatively evaluated at the semi-industrial facility metioned above. There, about 1.5 tons of eucalyptus chips were first comminuted to small particles with the size distribution shown by the curve A in Fig. 1, in order to make them suitable for irradiation with the 1.5MeV - 25mA Dynamitron Accelerator at IPEN's facilities. About one ton of that product was treated at 1.5×10^5Gy, and then, large samples of both, irradiated and non irradiated wood particles, were passed twice through the impact mill, giving the new size distribution represented by the curves C and B, respectively.

As can be deduced from these curves, 58% of the weight of irradiated wood sample comes from particles smaller than 300µm (50 Mesh, U. S. Series) while, for non irradiated wood sample, such particles represent only 30% of its weight. If the initial weight percentage corresponding to that particle size limit in the raw material is substracted from the above values, net increments of 37% and 9% are obtained. Thus, for the conditions of the test, grinding of irradiated wood renders a fourfold increase in the production of particles smaller than 300µm, as compared with non irradiated wood. On the other hand when equal weights of both samples were ground, operation time and mill power consumption diminished about 15% and 2%, respectively, in the case of irradiated wood.

Therefore, E.B. pretreatment of eucalyptus wood at an average dose of 1.5×10^5Gy, allows a reduction by a factor of almost five, in the grind-

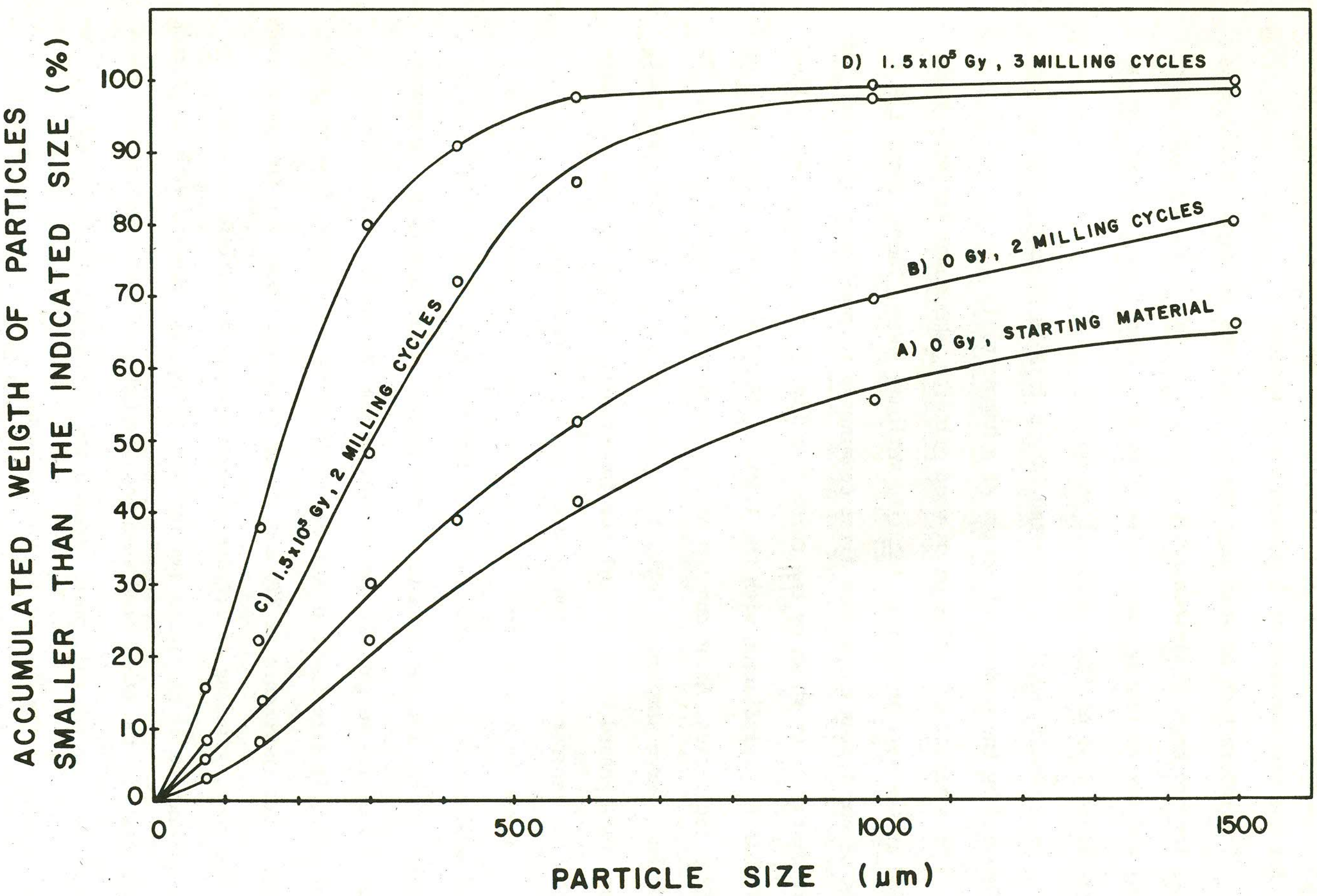

FIG. I - GRAIN SIZE DISTRIBUTION CURVES FOR WOOD POWDER PRODUCED BY HAMMER MILL PULVERIZATION OF IRRADIATED AND NON IRRADIATED EUCALYPTUS CHIPS.

ing energy required to produce a given weight of particles smaller than 300μm.

This result is higly promising in regard to the economic feasibility of large scale production of wood powder for any future application in the field of biomass conversion.

The large scale industrial irradiation of chips having thickness of about 3mm and lenght from 20 to 50mm (such as they are produced by log hogging machines) at the mentioned dosage, is technically possible if high energy-high current electron accelerator are used.

Theoretically, a 4MeV - 50mA machine could process about 5 tons of wood chips per hour, at 10^5Gy.

A preliminar cost analysis indicates that for the installation to be economically competitive it should be designed to treat, at least, 10 t/h of wood, assuming 35% of initial moisture content (on wet basis). This means that at least two accelerator of the above said characteristics should be used.

A tipical layout of such an installation is shown in Fig. 2.

3.0.0 EFFECT OF COMBINING E.B.P. WITH OTHER PRETREATMENTS, ON THE SACCHARIFICATION OF LIGNOCELLULOSIC MATERIALS.

E.B.P. at doses of at least 10^5Gy, combined with mechanical crushing at 50 Mesh and 2% NaOH impregnation (24 hours at room temperature) enhances the yield of reducing sugar obtained by enzymatic hydrolysis of eucalyptus wood and sugarcane bagasse, as shown by the bar graphs a) and b) of Fig. 3.

It can be noticed that while in both cases radiation alone (at 10^5Gy) has very little or no effect on the reducing sugar yield, the combination with alkali pretreatment increases markedly the efficiency of the enzymatic process.

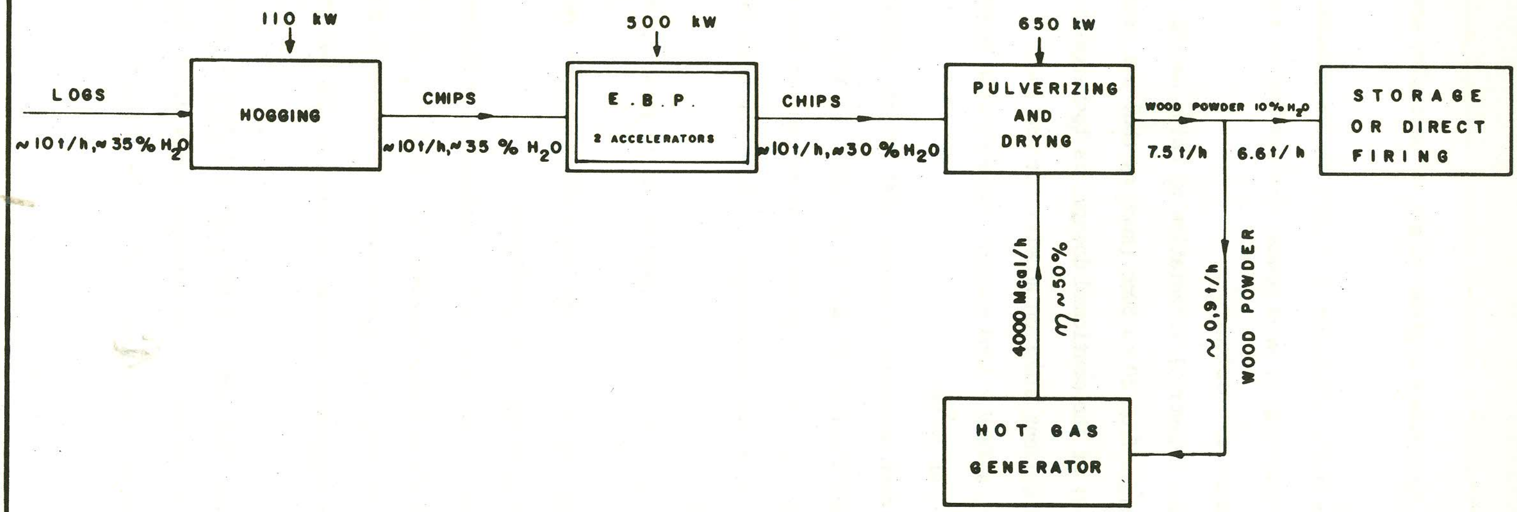

FIG. 2 - BLOCK-DIAGRAM OF A WOOD POWDERING SYSTEM USING E.B.P.

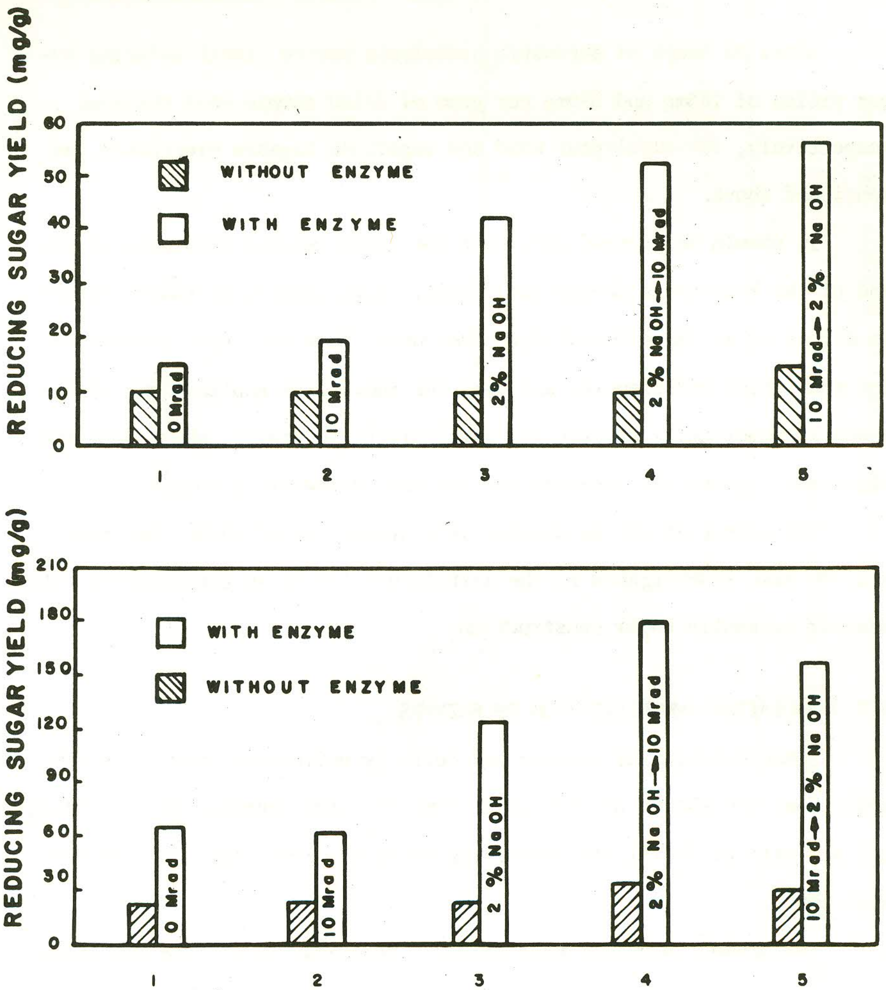

Fig 3 - Effect of different combinations of treatments on the reducing sugar yield

graph a) eucalyptus wood pulverized at 50 Mesh; 2h enzymatic hydrolysis at 50ºC; substrate: 10% w/v; enzyme: cellulase, 36 mg/ml.

graph b) sugarcane bagasse pulverized at 50 Mesh; 1 h enzymatic hydrolysis at same conditions as above.

After 48 hours of enzymatic hydrolysis period, total reducing sugar yields of 165mg and 390mg per gram of dried sample were obtained, respectively, for eucalyptus wood and sugarcane bagasse pretreated as mentioned above.

It should be pointed out, that the solid residue remaining at the end of the hydrolysis period has, itself, high commercial value, either as a fuel or as raw material for other uses. This fact may compensate low conversion efficiencies and make the industrial application of the process commercially attractive, particularly in Brazil, where wood and sugarcane bagasse are abundand and low cost renewable products.

The effect of EBP on diluted acid hydrolysis of these materials will be also investigated in the next future, using an experimental batch reactor presently under construction.

4.0.0 RADIATION IMMOBILIZATION OF ENZYMES

Immobilization of enzymes and cells by entrapping them in different types and shapes of unsoluble composites may increase their biological activity or facilitate recovering to reuse, improving the process efficiency.

Cellulase, an enzyme that converts cellulose in glicose, was chosen to initiate experiences at IPEN labs, on the application of radiation technology for the immobilization of bioactive materials.

The preliminary work was described in a progress report submitted to the IAEA, at the end of 1983 (5). Since then, further attempts were made to develop suitable techniques to immobilize cellulase, based on radiation induced polymerization of glass-forming monomers, at low temperature.

Double entrapping of enzymes by polymerizating an hydrophilic monomer in the presence of adsorbents such as powdered silica or additives as PEG (polyethylene glycol) seems to improve the immobilization effi -

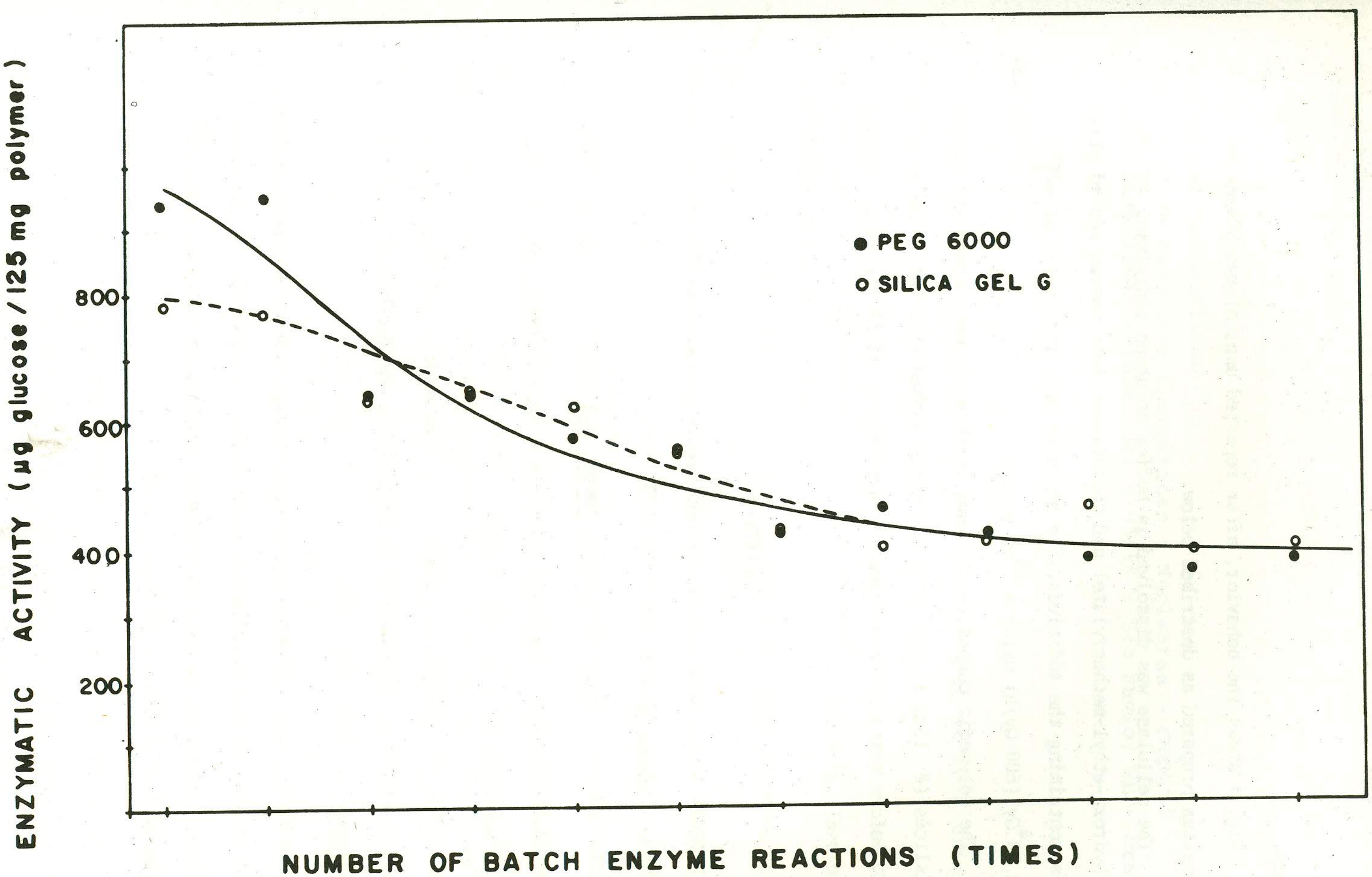

FIG. 4 - RELATIONSHIP BETWEEN NUMBER OF BATCH ENZYME REACTION AND ACTIVITY YIELD OF IMMOBILIZED CELLULASE. SUBSTRATE: 1% CMC. BIOCOMPOSITE: 2.4 ml NOVO CELLULASE (115 mg PROTEIN/ml); 1.6 ml HEMA; 1g ADDITIVE (PEG OR SILICA GEL G).

ciency.

Fig. 4 shows the behavior, after repeated use, of two bioactive composites prepared as described below.

The cellulase was dissolved in buffer solution containing 40% HEMA (hydroxi-ethyl-methacrylate) and conditioned into vaccum sealed glass tubes containing the additives. The ampoules were irradiated at $-78^{o}C$ with 10^4Gy (600 Gy/h) using a ^{60}Co source.

The polymeric composite obtained in this way was frozen and sliced. The slices (Ø 13mm x 1mm) were throughly washed with water and dried at $37^{o}C$, before testing their enzymatic activity on 1% CMC (carboxy methyl cellulose) solution.

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