THERMAL ANALYSIS – A TOOL FOR ILLUSTRATING MIXED POLYMER COMPOSITION

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A mixture of PVA (Polyvinyl Alcohol) and CMC (Carboxymethyl Cellulose) polymer solution was prepared and treated for obtaining a polymer carrier for enzyme immobilization. The leakage in water of the mixed solid obtained by the cryogel technique was monitored using UV-Vis spectroscopy for the water solutions and the thermal analysis for the solid polymer.

The thermal analysis proved to be a good tool for evidencing the CMC leakage.

Keywords: cryogel polymer, PVA, CMC, thermal analysis

1. Introduction

The sustainable development imposes the application of new, green technologies with diminish polluting effects [1]. The new Europe 2020 strategy has created a framework for achieving an ambitious series of goals – economic, social and environmental – by the end of this decade [2].

Among other solutions, a good way for an economy which depends less on fossil for energy and raw materials is the large scale application of biotechnology. The use of enzymes as catalysts for different processes leads to economy of energy and a reduce quantity of wastes [3, 4].

The industrial application of enzymes causes some problems in connection with the stability of these catalysts. A solution to this problem consists in immobilizing the enzymes [5, 6].

The improvement of the enzyme quality by an immobilization process depends of the carrier properties [5]. Thus, attempts to obtain new carriers are of interest. A mixed cryogel polymer has been obtained from CMC and PVA and its stability in water solution tasted by UV-Vis spectroscopy and thermal analysis

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2. Experimental

Materials

Granulated PVA (M = 61,000 g mol^{-1}, degree of hydrolysis 98 – 99%) and CMC as sodium salt (M = 90,000 g mol^{-1}) have been purchased from Sigma-Aldrich. The other reagents were of analytical grade purity.

Methods

The synthesis of the mixed cryogel was realized according the procedure described by Xiao and Gao [7]. Granulated PVA (5 g) was dissolved in 90 mL distilled water, with stirring, at 50 °C for 2 h. In the obtained solution 5 g of sodium salt of CMC was added in 10 min., with stirring and the mixture was kept at the same temperature for another hour, for homogenization. After cooling, the solution was slowly pored, in 6 rectangular molds, and frozen at -18 °C, for 12 h. The solid obtained was thawed at 4 °C for another 12 h. The cycle was repeated again for 2 times. The white solid was immersed into a solution of $CuSO_4$ (0.5 M) for 5h. The resulted polymer has a deep blue color.

The stability in water was monitored as follows. The polymer resulted after treatment with $CuSO_4$ solution, was treated 4 times with 50 mL of distilled water. In the first treatment, pieces of cryogel were immersed in distilled water and kept under magnetic stirring for 30 min. The second and third times, pieces of cryogel were immersed in distilled water and kept for 24 h. The fourth time the criogel pieces were held three days immersed in distilled water. The solutions from each water treatment cycle were separated by decantation and analyzed by UV-Vis spectrometry.

The UV-Vis spectra have been acquired at a JASCO V560 spectrophotometer with 10 mL cuvettes, in the domain 200–900 nm, with a speed of 200 nm min^{-1}.

The thermal analyses were performed with a Netzsch 449C STA Jupiter. Samples were placed in alumina crucible and heated with 10 K min^{-1} from room temperature to 900 °C, under the flow of 20 mL min^{-1} dried air.

3. Results and Discussion

The new carrier obtained by the previously described method is a blue solid, containing both polymer components the PVA and CMC. The Cu^{2+} ions are linked to the CMC structure, substituting partially the Na ions (see Fig. 1).

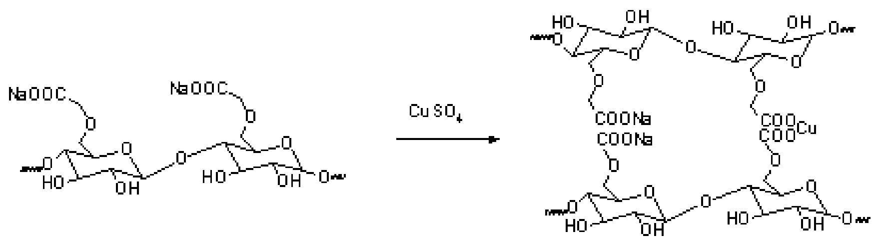

Fig. 1 Cross linked CMC polymer

The cryogel type method was chosen due to the quality of the obtained polymers, such as [7-10]:

- Macro-porosity (micrometer-sized pores);
- Mechanical resistance;
- Nontoxic effects due to lack of monomers which remain in the water solution, etc.

The PVA polymer gives resistant net due to the inter-chain hydrogen bonds. The CMC component is introduced for attaching Cu^{2+} ions [8] which may link the enzyme by coordination [9].

The presence of the two type polymers into the resulted cryogel is confirmed by the thermal behavior of it in comparison with each of the two components (see Fig. 2 a-c).

a b

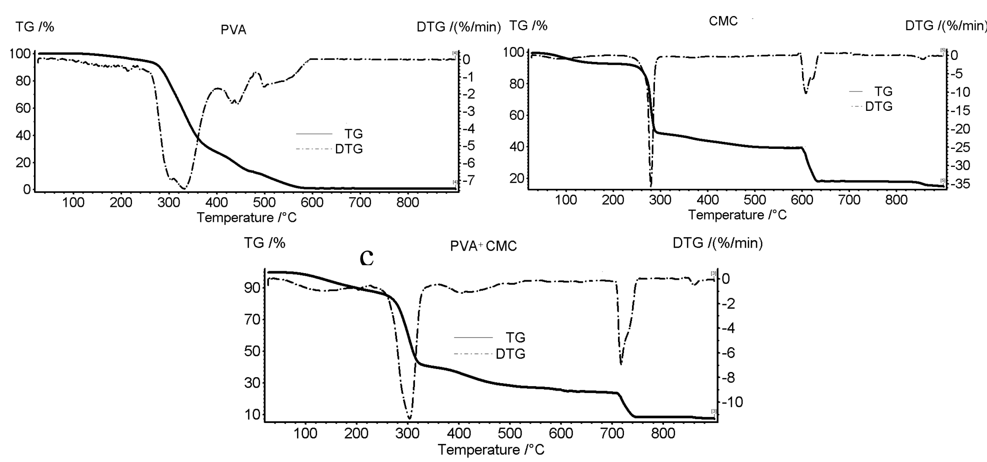

Fig. 2 Thermal behavior of polymers: a) PVA; b) CMC; c) cryogel polymer PVA+CMC

From the aspect of Fig. 2c the presence of both polymer components, the polyvinyl polymer (PVA) and the poly-carbohydrate (CMC) is obvious the DTG curve containing peaks summing up the peaks from 2a and 2b Figs.. It is worthwhile mentioning that the resulted DTG curve is not only a sum of both components, a stabilization being observed by displacement of the peak from 610 °C in CMC to 720 °C in the mixture of polymers. This result may be explained by formation of hydrogen bonds between the two polymers due to the numerous OH groups presented in both components.

The addition of the copper salt changed the aspect of the thermal behavior of the polymer mixture, as shown in Fig. 3.

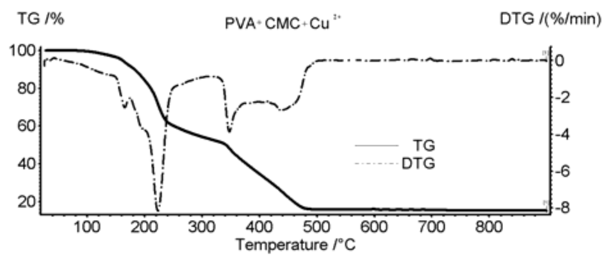

Fig. 3 Thermal behavior of copper salt treated cryogel polymer PVA+CMC

The curve aspect suggests the formation of inter-chains copper bonds inducing a different behavior to the resulted polymeric net. The presence of copper is confirmed also by the higher residue obtained, 14.9 % for the copper salt treated polymer mixture, compared with 7.4 % the value obtained for the untreated polymer mixture. This residue is due to the metallic oxide obtained in the oxidation process.

The resulted solid acts no more like a sum of the two components but as a new different polymer where both components have a strong interaction. According the experimental results the copper derivative is less stable in comparison with the sodium one, all the DTG peaks being moved to lower temperature values. It is difficult to identify each of the cryogel components, the curve aspect from Fig. 3 being different from the curves of component polymers (Figs. 2a and 2b) as well as from the mixture of it (Fig. 2c).

For the application of the cryogel polymer as enzyme carrier, the stability of it is essential. Thus, the behavior in water solution was considered for the copper treated polymer. The polymer was immersed in distilled water repeatedly, during 5 days.

The possible leakage of parts of the mixed solid was evidenced after each immersion, by UV-Vis analysis of the water solutions, as well as the monitoring of the composition of the polymer by thermal analysis.

The results are presented below (see Figs. 4 and 5).

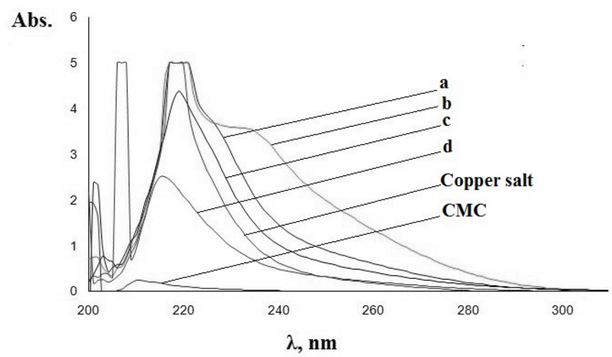

Fig. 4 UV-Vis spectra of CMC and $CuSO_4$ water solutions, as well as of the solutions resulted from water immersion of the cryogel polymer (a – first, b – second, c – third, d – fourth time)

The UV-Vis spectra of the water solutions obtained after the polymer immersion superpose on the UV-Vis spectra of the sodium salt of CMC solution, as well as the copper salt ($CuSO_4$) solution.

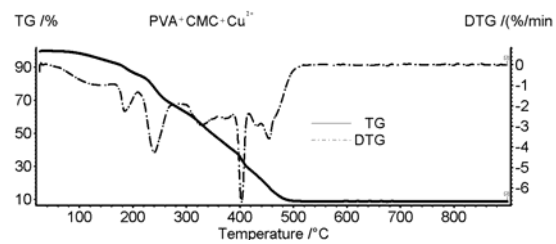

Fig. 4 Thermal behavior of water treated cryogel polymer

The new DTG curve shows the disappearance of some peaks which may be attributed to the leakage of CMC sodium derivative, as well as the adsorbed copper salt ($CuSO_4$), both being water soluble. The water solubilization of these components is illustrated also by the diminishing of the metallic oxide residue from the initial value of 14.9 % to 8.4 %. The fading of the blue color also confirmed the copper migration to the water solution. The IR spectra are in agreement with such assertion, a decrease of the CO band (1610 cm^{-1}) characteristic to glucose ring [11] being observed.

4. Conclusions

A new cryogel polymer was produced from a mixture of CMC as sodium salt and PVA.

The thermal analysis is an appropriate tool to study the composition of the obtained cryogel polymer.

The addition of copper ions changed totally the thermal behavior of the mixed polymer due to a stronger interaction between components.

The new cryogel type polymer is not stable in water a leakage of both CMC component and copper ions being evidenced by the experimental results. Thus, the cryogel polymer is not suitable for an enzyme carrier application. Application as chromatographic stationary phase may be recommended.

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REFERENCES

[1] *UNEP* ”Towards Greener & More Inclusive Economies”, http://www.unep. org/green economy/Portals/88/documents/GEI%20Highlights/GE_flyer_October27_web-ready.pdf
[2] *The European Association of Bioindustry,* EuropaBio Policy Guide Building a Bio-based Economy for Europe in 2020, www.europabio.org, www.bio-economy.net.
[3] *A. Liese, K. Seelbach, A. Buchholz, J. Haberland*, “Processes” in Industrial Biotransformations. A. Liese, K. Seelbach, C. Wandrey (Eds.), 2nd edition, 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, pp. 147-514.
[4] *S. J. Charmock, B. V. McCleary*, Les enzymes : Applications industrielles et analytiques, Revue des Œnologues, **116**, 2005, 11-15.
[5] *L, Cao.* Carrier-bound Immobilized Enzymes: Principles, Application and Design, 2005 Wiley-VCH Verlag GmbH & Co. KgaA, Weinheim.
[6] *B. M. Brena*, *F. Batista-Viera*, “Immobilization of enzymes – a literature survey” in Methods in biotechnology: immobilization of enzymes and cells, J. M. Guisan (Ed), 2006 Humana Press Inc., Totowa, N.J., USA, pp. 15–30.
[7] *C. Xiao, Y.Gao*, Preparation and Properties of Physically Crosslinked Sodium Carboxymethylcellulose/Poly(vinyl alcohol) Complex Hydrogels, J. Appl. Polymer Sci., **107**, 2008, 1568–1572.
[8] *I. M. Jipa, A. Stoica Guzun, M. Stroescu*, Controlled release of sorbic acid from bacterial cellulose based mono and multilayer antimicrobial films, LTW Food Sci. Technol., **47**, 2012, 400-406.
[9] *M.D. Stanescu, S. Gavrilas, R. Ludwig, D. Haltrich, V.I. Lozinsky,* Preparation of immobilized *Trametes pubescens* laccase on a cryogel-type polymeric carrier and application of the biocatalyst to apple juice phenolic compounds oxidation. Eur. Food Res.Technol., **234**, 2012, 655–662.
[10] *V.I. Lozinsky*, “A Brief History of Polymeric Cryogels” in Polymeric Cryogels, Advances in Polymer Science 263, O. Okay (Ed.), 2014 , Springer International Publishing, Cham, Switzerland, pp. 1-48.
[11] *J. Wang, P. Somasundaran*, Adsorption and conformation of carboxymethyl cellulose at solid–liquid interfaces using spectroscopic, AFM and allied techniques. J. Colloid Interf. Sci., **291**, 2005, 75–83