Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Preparation, Characterization and Luminescence Study of Chitosan Membrane and Powder Forms with Eu^{3+} and Tb^{3+}

Roseane S. Oliveira[a]; Danielle O. Maia[a]; Márcia R. Pereira[a]; Fabiana R. G. E. Silva[a]
[a] Departamento de Química, Universidade Federal do Rio Grande do Norte, Campus Universitário, Lagoa Nova, Natal, Brazil

To cite this Article Oliveira, Roseane S. , Maia, Danielle O. , Pereira, Márcia R. and Silva, Fabiana R. G. E.(2010) 'Preparation, Characterization and Luminescence Study of Chitosan Membrane and Powder Forms with Eu^{3+} and Tb^{3+}', Journal of Macromolecular Science, Part A, 47: 5, 392 — 398

To link to this Article: DOI: 10.1080/10601321003659457

URL: http://dx.doi.org/10.1080/10601321003659457

Journal of Macromolecular Science, Part A: Pure and Applied Chemistry (2010) **47**, 392–398

ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601321003659457

Preparation, Characterization and Luminescence Study of Chitosan Membrane and Powder Forms with Eu^{3+} and Tb^{3+}

ROSEANE S. OLIVEIRA, DANIELLE O. MAIA, MÁRCIA R. PEREIRA and FABIANA R.G. E SILVA*

Departamento de Química, Universidade Federal do Rio Grande do Norte, Campus Universitário, Lagoa Nova, Natal, Brazil

Received, Accepted October 2009

Chitosan membranes with trivalent lanthanide ion Eu^{3+} were prepared at a ratio of 3:1 w/w (chitosan:lanthanide). There was no membrane formation at a ratio of 1:1 w/w (chitosan: Eu^{3+} or Tb^{3+}); in this case a white solid powder was obtained. Both chitosan compounds were characterized by elemental analysis (CHN), thermal analysis (TG/DTG), scanning electron microscopy (SEM) and luminescence spectroscopy. CHN analysis was performed only for chitosan compounds in powder form, suggesting that these compounds have the general formula $QUILn.6H_2O$, where QUI = Chitosan and Ln = Eu^{3+} or Tb^{3+}. The results of TG/DTG curves for chitosan membranes with Eu^{3+} ion indicate that the introduction of this metal into the chitosan structure causes gradual degradation in residual carbons, showing lower weight loss in the Eu^{3+} membranes compared to pure chitosan membrane. Analysis of luminescence demonstrated that chitosan membranes with Eu^{3+} ion exhibit emission in the visible region, showing emission bands from chitosan and Eu^{3+} moieties. For chitosan with Eu^{3+} and Tb^{3+} ions compounds, in powder form, the analysis of luminescence suggested that chitosan is not transferring energy to the lanthanide ion; however, the chemical region where the lanthanide ion is found breaks the selection rules and favors the emission of these ions.

Keywords: Chitosan, membrane, lanthanide, luminescence

1 Introduction

Much has been studied and written about chitosan, a natural and linear copolymer of β-(1→4)-2-amino-2-deoxy-D-glucopiranose and β-(1→4)-2-aceto-amido-2-deoxyglucopiranose, derived from chitin (1). However, the physical and chemical properties of chitin and of its N-deacetylated (chitosan) derivatives are very different; for example, the chitin has a lower solubility compared to chitosan. Because it is natural, biodegradable, extremely abundant and non-toxic, chitosan has been proposed as a potentially attractive material for several uses, mainly in engineering, biotechnology and medicine. It is also commonly indicated for use as a complexing agent of metallic ions (2). Commercial chitosan generally has a degree of deacetylation (DD), varying between 70% and 95%, with molar mass in the 10^4-10^6 $g.mol^{-1}$ range. Since most of the properties of this polysaccharide are intimately related to these two parameters (3), their determination is indispensable. Thus, the precise knowledge of the content of N-deacetylated (DD) groups and consequently, of NH_2 groups, is important in characterizing any chitosan deacetylation process, as well as any other chemical modification (4).

Studies have been done related to the membrane formation with divalent and trivalent metal ions (5–8). A weak complexation of the chitosan with the lanthanide ion was observed (9). The interaction between Cu^{2+} and chitosan was studied in aqueous solution at different pH values, and it was observed that this complex has a hydroxyl-bridged structure (10). Besides, the application of the chitosan membrane with metal ion to the treatment of liquid waste (11) was investigated. Research involving the environmental toxicology shows the application of chitosan in the adsorption of metal ions as europium (Eu^{3+}) (12). In the present study, the synthesis, characterization and luminescence analysis of the pure chitosan and chitosan with Eu^{3+} and Tb^{3+} were carried out.

Some trivalent lanthanide ion compounds have suitable properties to act as structural and analytical probes in live and chemical systems. When excited in the ultraviolet region, they display intense luminescence, giving rise to narrow atomic bands corresponding to the 4f-4f transitions in the central ion (13). The f-f transitions are electric dipole-forbidden since there are no changes in parity (Laporte's rule), but the influence of the ligand field is

---

*Address correspondence to: Fabiana R.G. e Silva, Departamento de Química, Universidade Federal do Rio Grande do Norte, Campus Universitário, Lagoa Nova, CEP 59.072-970, Natal - RN, Brazil. Tel.: 55 84 32153828; Fax: 55 84 32119224; E-mail: fabiana.goncalves@quimica.ufrn.br; fabiana.goncalves@ufrnet.br

sufficient to promote a small parity mixture in the states, relaxing Laporte's rule and thus allowing f-f transitions to occur by the forced electric dipole mechanism, although at low intensity (14). Eu^{3+} and Tb^{3+} based luminescent probes are especially efficient, owing to the long lifetime of their excited states ($^5D_0$ and $^5D_4$, respectively). It has been recently shown (15) that trivalent lanthanide ions can be incorporated within the organic ligands. In this study, the lanthanide ion is incorporated into chitosan, to form membranes where the lanthanide ion is adsorbed into the chitosan structure.

This study aims to obtain hybrid organic material (chitosan) and inorganic (lanthanide ion) with luminescent properties, so they can have their application as luminescent probes. The synthesis, characterization and study of luminescence were performed to obtain new materials with different proportions of chitosan/lanthanide, ranging from the polymeric membranes to the compounds in the powder form.

2 Experimental

2.1 Materials

The substances used as reagents and solvents in the synthesis of membranes and chitosan compounds with lanthanide ions (Ln^{3+}) were: Chitosan – Polymar Ltd, DD = 85% and MW(g/mol) = 2.9×10^5; Acetic acid – Chromate Chemicals Ltd (99.5%); Sodium hydroxide – Vetec Fine Chemicals Ltd (98.00%); Europium oxide – Spectrum Chemical Corp (99.99%); Terbium oxide – Spectrum Chemical Corp. (99.99%).

2.2 Chloride Preparation

The lanthanide chlorides were prepared as follows: HCl (1:1) was added dropwise to an aqueous suspension of lanthanide oxide (Eu_2O_3 and Tb_4O_7) until complete dissolution. The pH was controlled in the 2–3 range. The solution was diluted with distilled water and then evaporated in double boiler at 50°C.

2.3 Preparation of Chitosan Membranes with Eu^{3+} ion

The membranes were obtained from the reaction between chitosan and lanthanide chloride ($EuCl_3.xH_2O$), at a ratio of 3:1 weight/weight (w/w) using the casting method. Chitosan was dissolved in an aqueous solution of 3% acetic acid under constant agitation for 24 h. The chitosan solution was vacuum filtered with a nylon screen filter and, later, with a Milex Millipore filter ® with a porous diameter of 41μm. Lanthanide chloride ($EuCl_3.xH_2O$) was then added to the chitosan solution and kept under agitation for 6 h at ambient temperature to obtain homogeneous salt. During each hour of reaction, an aliquot of 25 mL was removed from the solution, placed in Petri dishes and stored in an oven for 24 h for total evaporation of the solvent and membrane formation. The membranes were obtained at 1, 2, 3, 4, 5 and 6 h of reaction. These membranes were neutralized with a solution of 5% NaOH for 2 h and washed with distilled water to eliminate the salts and sodium hydroxide residue. The membranes were then placed on an extensor to dry.

2.4 Characterization

The percentages of carbon, hydrogen and nitrogen (C, H, N) were determined using a Carla Erba 1110 CHN Elemental Analyzer. The TG/DTG curves for the thermoanalytical study of the chitosan membranes with Eu^{3+} ion at a ratio of 3:1 were obtained using a Shimadzu TGA-50 thermobalance under dynamic atmosphere of N_2, with a heating rate of 5°C min^{-1}. The excitation and emission spectra of the chitosan compounds were obtained using a Shimadzu RF-5301PC spectrofluorimeter and John-Yvon Ramonor U-1000 spectroanalyzer, respectively. The excitation measurements were performed in the solid state, fixing $\lambda em = 460$nm for pure chitosan membrane and $\lambda em = 540$ nm for chitosan compound with Tb^{3+} ion, whereas the value for membrane and chitosan compound with Eu^{3+} ion was $\lambda em = 612$ nm. Emission measurements were also conducted in solid state, fixing excitation at the wavelength with highest intensity in the excitation spectrum, for both chitosan membrane and powder forms. SEM photographs of cross section and surface of membranes coated with gold were taken using a scanning electron microscope, Model: JEOL JSM 5800CV.

3 Results and Discussion

3.1 Complexometric Titration

Complexometric titration was carried out for chitosan compounds with Eu^{3+} and Tb^{3+} ions. Titration showed a percentage of metal in the chitosan structure. As expected, Table 1 presents the results of this analysis, indicating that chitosan compounds with Eu^{3+} and Tb^{3+} ions have a ratio of 1:1 w/w (lanthanide:chitosan).

Table 1. Results of complexometric titration of chitosan compounds under powder form

	Metal (%)	
Compounds	*Theor.*	*Exp.*
QUI + Eu $^{3+}$	28.87	28.87
QUI + Tb^{3+}	28.73	29.66

Table 2. Theoretical and experimental results of CHN analysis for chitosan compounds with Tb^{3+} and Eu^{3+} ions under powder form

	Carbon (%)		*Hydrogen (%)*		*Nitrogen (%)*	
Compounds	*Theor.*	*Exp.*	*Theor.*	*Exp.*	*Theor.*	*Exp.*
QUI	44.72	38.73	6.87	6.36	8.69	7.16
QUI + Eu^{3+}	13.47	11.64	4.36	3.97	2.65	1.07
QUI + Tb^{3+}	13.47	13.08	4.30	3.93	2.62	1.45

3.2 CHN Analysis

Elemental analysis of CHN is quite useful in determining a possible molecular formula for the product of a chemical reaction. Table 2 shows the theoretical and experimental results of CHN analysis for chitosan compounds under the powder form, obtained at a ratio of 1:1 w/w, suggesting that these compounds have a general formula $QUILnCl_3.6H_2O$, where QUI = chitosan and Ln = Eu or Tb. It is suggested that the difference between the theoretical and experimental values is due to the deacetylation degree of chitosan which, in the case of pure chitosan and of compounds with lanthanides, still has a small fraction of chitin.

3.3 Thermal Analysis

3.3.1. *Thermal analysis for the membranes of pure chitosan and chitosan with* Eu^{3+}

Figures 1 and 2 show TG/DTG curves for membranes of pure chitosan and chitosan with Eu^{3+} ion. The curve of the membrane with Eu^{3+} ion is different from the pure chitosan curve. The results of the TG/DTG curves show that the first stage, correspondent to water loss, is basically equal for the two cases. The second stage presents a difference in weight loss for the two curves. This indicates that the Eu^{3+} ion is introduced in the chitosan structure (16). The weight loss in the second stage indicates the depolymerization and decomposition of the acetylated and deacetylated units of the polymer, as previously described (12). Table 3 shows weight loss for the membranes of pure chitosan and chitosan with Eu^{3+} ion. In the second stage, the weight loss of the Eu^{3+} membrane is around 25% smaller, indicating that the Eu^{3+} ion hinder the bond break of the polymer, due the interaction between chitosan and this ion. The third stage, that is not present in the pure chitosan membrane, correspond to the chitosan moiety bonded to the Eu^{3+} ion.

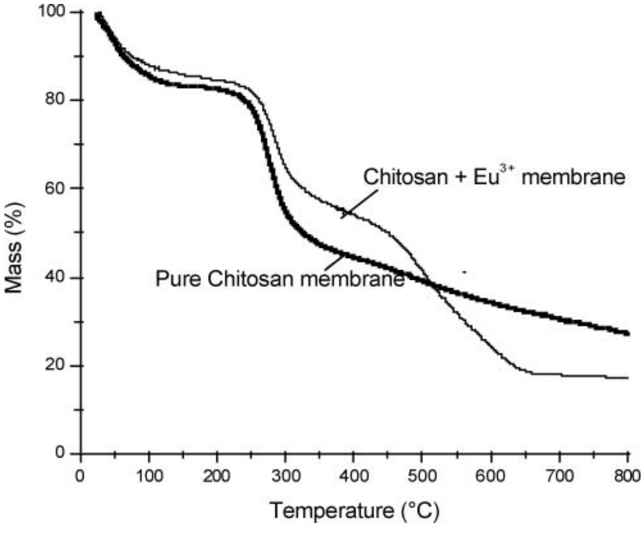

Fig. 1. TG curves for pure chitosan membrane and chitosan with Eu^{3+} ion.

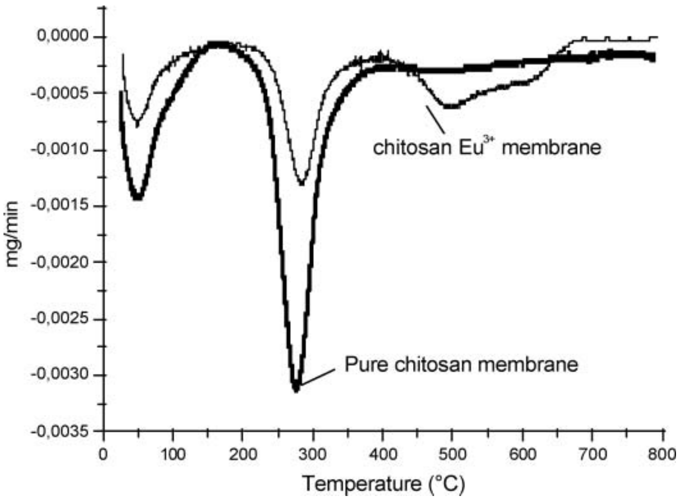

Fig. 2. DTG curves for pure chitosan membrane and chitosan with Eu^{3+} ion.

3.3.2. *Thermal analysis of the chitosan compound with* Tb^{3+} *and* Eu^{3+} *ions in the powder form*

Figure 3 and 4 illustrate TG/DTG curves for chitosan compounds under membranes and powder forms. Some differences can be observed among the three curves. It is important to point out that these curves were obtained using different mass. The first peak, in the DTG curve, is more intense for Tb compound due to hydration water in its structure. There are three stages of weight loss for the membrane, while the compounds present four stages. The first weight loss corresponds to water loss for the three cases. The third weight loss is only observed in the chitosan compound with Eu^{3+} and Tb^{3+} ion. This stage and the second weight loss on the TG curve of the chitosan compounds with Eu^{3+} and Tb^{3+} ion indicate that europium and terbium chloride were introduced into the chitosan structure, suggesting that both the Eu^{3+} and Tb^{3+} ion hinder polymer bond breaking. This may occur because of some type of interaction taking place between the chitosan and the Eu^{3+} and Tb^{3+} ions, changing the polymer structure (16). The

Table 3. Weight loss for the membranes of pure chitosan and chitosan with Eu^{3+}

	Weight loss (%)					
	1st stage		*2st stage*		*3st stage*	
Membrane	*Weight (%)*	*Temp.(°C)*	*Weight (%)*	*Temp.(°C)*	*Weight (%)*	*Temp.(°C)*
QUI	15.11	45	39.28	305	—	—
QUI + Eu^{3+}	14.36	37	29.72	310	35.72	567

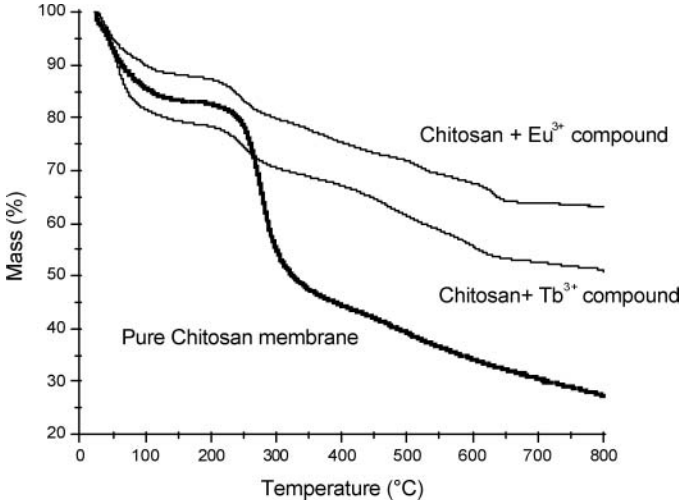

Fig. 3. TG curves of chitosan compounds under membrane and powder form.

fourth weight loss, that is also not present in pure chitosan membrane, shows a small loss weight for Eu^{3+} and Tb^{3+} chitosan, corresponding to lanthanide residue.

3.4 Luminescence Analysis

3.4.1. *Luminescence analysis of pure chitosan membrane*

The emission spectrum of chitosan, (Fig. 5) fixing $\lambda\text{exc} = 369$ nm, shows a broad band at 465 nm with respect to chitosan transitions (17). Chitosan has a relatively high intensity in the visible region, with energy of 21 505 cm^{-1} ($\lambda\text{em} = 465$ nm), indicating that this bonding potential may serve as an antenna for transferring energy to trivalent lanthanide ions (Ln^{3+}) in compounds of Ln^{3+} with chitosan.

3.4.2. *Luminescence analysis of chitosan membrane with Eu^{3+}*

Table 4 shows the transitions observed in the excitation spectra of chitosan membranes with Eu^{3+} ion. It was observed that the membranes with Eu^{3+}, obtained at 1, 2, 3, 4, 5 and 6 h, exhibited excitation in the same excitation region of the chitosan. This explains why both

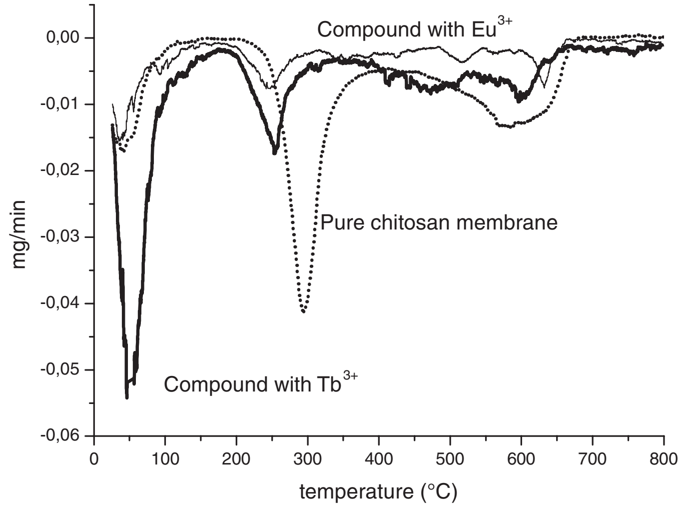

Fig. 4. DTG curves of chitosan compounds under membrane and powder form.

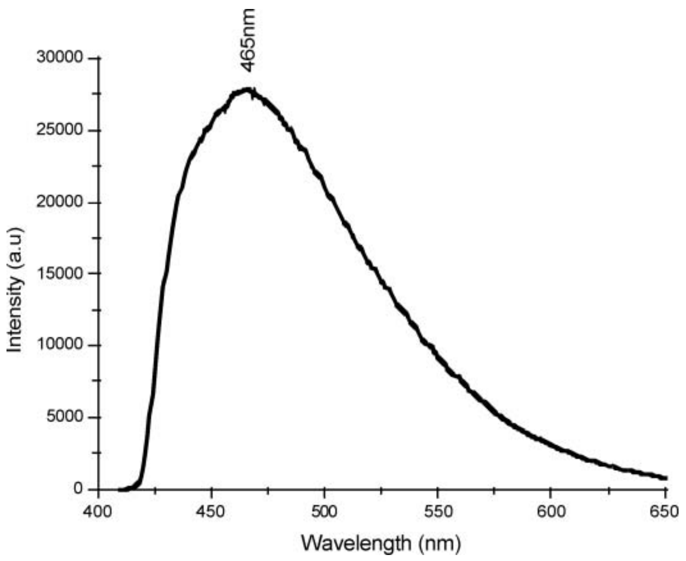

Fig. 5. Emission spectrum of chitosan, fixing $\lambda_{exc} = 369$ nm.

Table 4. Excitation spectrum transitions of chitosan membrane with Eu^{3+} ion, obtained at 1, 2, 3, 4, 5 and 6 h

Membrane	*λ(exc)*	*Transitions*
QUI + Eu^{3+} (1 h)	355nm	$^7F_0 \rightarrow {}^5L_{10}$
	330nm	$^7F_1 \rightarrow {}^5H_7$
QUI + Eu^{3+} (2 h)	358 nm	$^7F_0 \rightarrow {}^5D_4$
QUI + Eu^{3+} (3 h)	308 nm	$^7F_0 \rightarrow {}^5F_2$
QUI + Eu^{3+} (4 h)	368 nm	$^7F_0 \rightarrow {}^5L_8$
QUI + Eu^{3+} (5 h)	353 nm	$^7F_0 \rightarrow {}^5L_{10}$
QUI + Eu^{3+} (6 h)	354 nm	$^7F_0 \rightarrow {}^5L_{10}$

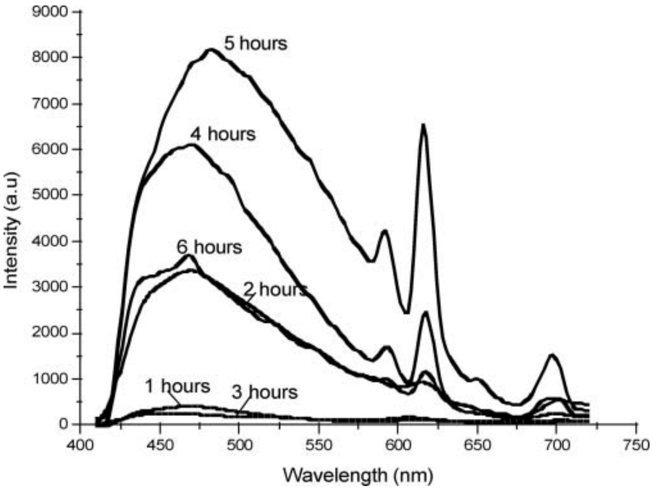

Fig. 6. Emission spectra of chitosan membrane with Eu^{3+} ion, fixing $\lambda_{exc} = 382$ nm for the spectrum at 1 h, $\lambda_{exc} = 358$ nm for 2 h, $\lambda_{exc} = 308$ nm for 3 h, $\lambda_{exc} = 368$ nm for 4 h, $\lambda_{exc} = 353$ nm for 5 h and $\lambda_{exc} = 354$ nm for 6 h.

Eu^{3+} and chitosan emissions are observed in the emission spectra of these membranes. The transitions presented in Table 4 were identified using the energy levels diagram of the Eu^{3+} ion in LaF_3, with their respective electronic states (18,19). Figure 6 shows the overlap of emission spectra of chitosan membranes with Eu^{3+} ion at 1, 2, 3, 4, 5 and 6 h. Except for Eu^{3+}chitosan membrane at 1 h, that was excited in the chitosan band, all the membranes were excited directly in the Eu^{3+} ion transitions, as could be observed in Table 4. The overlap in Figure 6 shows that the transitions related to Eu^{3+} ion appear in all emission spectra of chitosan membranes with Eu^{3+} ion, with membranes at 1 and 3 h showing the lowest emission intensities. The f-f transitions are forbidden by selection rules (20), but the chemical environment in which the lanthanide ion is located in the membrane allows these transitions to occur and, therefore, be observed in the emission and excitation spectra.

3.4.3. *Luminescence analysis of chitosan compounds with Tb^{3+} and Eu^{3+} ions*

The excitation spectra of the chitosan compound with Tb^{3+} ion, with λem = 540 nm, present some peaks with narrow lines from the lanthanide ion at 234, 285, 356, 371 and 381 nm. These four last excitation wavelengths are attributed to $^7F_6 \rightarrow {}^5F_5$, $^7F_6 \rightarrow {}^5D_2$, $^7F_6 \rightarrow {}^5G_6$ and $^7F_6 \rightarrow {}^5D_3$ transitions, respectively (18,19). It is suggested that the 234 nm (42 735 cm^{-1}) peak of high energy is from the charge transfer band of the ligand to metal (21), since this peak is neither present in free Eu^{3+} ion nor in pure chitosan. Emission spectra of the chitosan compound with Tb^{3+} ion

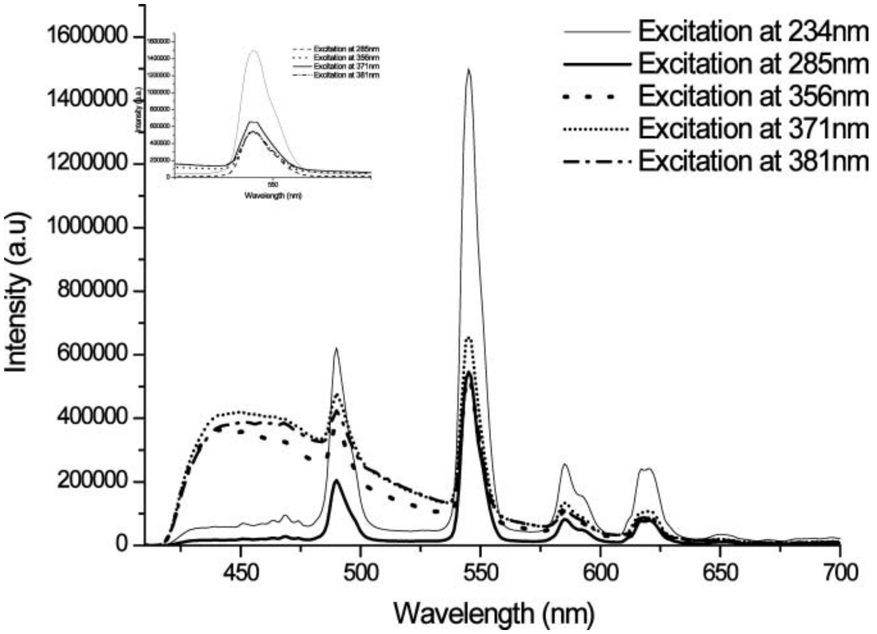

Fig. 7. Emission spectra of the chitosan compound with Tb^{3+} ions, with $\lambda_{exc} = 234$ nm, 285 nm, 356 nm, 371 nm and 381 nm. The window shows an enlargement of the region between 525 and 577 nm, with upper limit intensity at 7×10^6 a.u.

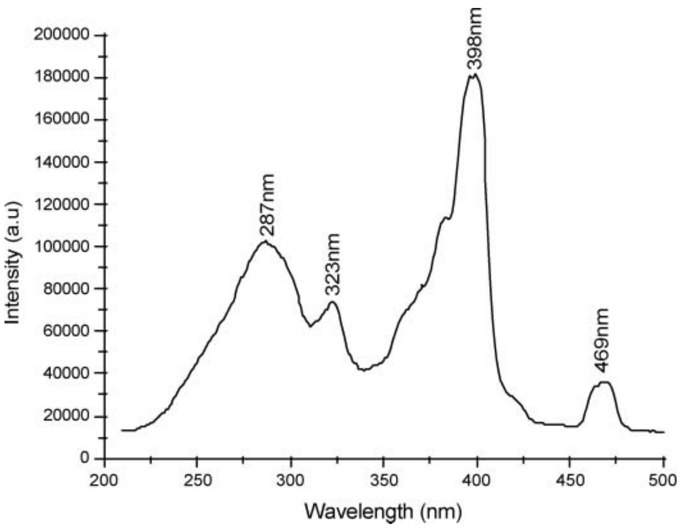

Fig. 8. Excitation spectra of the compounds of chitosan with Eu^{3+} under powder form.

were obtained fixing λexc at several wavelengths (234 nm, 285 nm, 356 nm, 371 nm and 381 nm) observed in the excitation spectrum. Figure 7 shows the overlap of the emission spectra obtained with these excitation wavelengths. All five emission spectra had four well defined peaks at 489 nm, 543 nm, 585 nm and 620 nm, related to transitions $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$ of the Tb^{3+} ion (18,19), respectively. Because transition $^5D_4 \rightarrow {}^7F_5$ has greater intensity and is more influenced by the ligand field, it is considered hypersensitive, showing green emission. The emission spectra with λexc = 356 nm, 371 nm and 381 nm also exhibit a broad band related to chitosan transitions (17), given that the excitation wavelengths on these emission spectra also excite the chitosan, as observed on pure chitosan membranes and powder. The observation of transitions related to the Tb^{3+} ion, in both emission and excitation spectrum, indicates that the chemical environment where the lanthanide ion is found breaks the selection rules and favors Tb^{3+} ion emission. We conclude that energy transfer from chitosan to Tb^{3+} ion is not occurring, given that different spectra were obtained in terms of band number and peak emissions for different λexc. Meanwhile, the peak in 234 nm, attributed as charge transfer band, produces the highest emission intensity.

The excitation spectra of the chitosan compound with Eu^{3+} ion under powder form, Figure 8, obtained fixing λem = 612 nm, shows four peaks at 287, 323, 398 and 469 nm. These two last excitation wavelengths are attributed to $^7F_0 \rightarrow {}^5L_6$ and $^7F_0 \rightarrow {}^5D_2$ transitions characteristic of Eu^{3+}, respectively (18,1). However, the peaks of high energy at 287 and 323 nm can be, as on Tb compound, charge transfer bands of the ligand to metal due the Eu interaction with the OH or NH_2 donor group of the chitosan (16, 21).

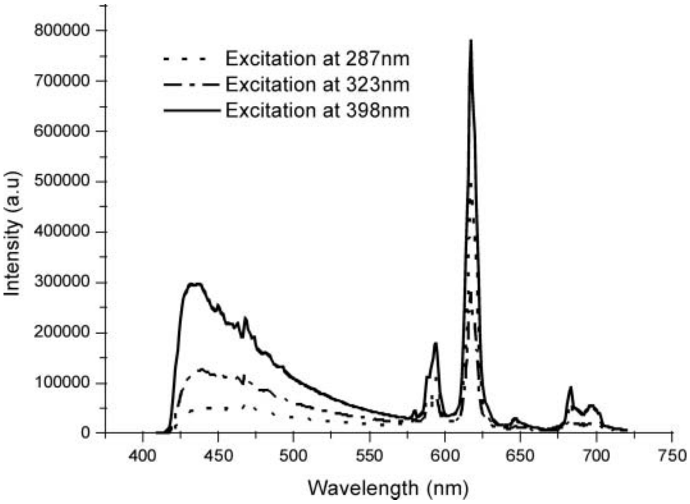

Fig. 9. Emission spectra of (the) chitosan compound with Eu^{3+} ion under powder form, with $\lambda_{exc} = 287$ nm, 323 nm and 398 nm.

The emission spectra of chitosan compound with Eu^{3+} ion were obtained fixing λexc in three wavelengths (287 nm, 323 nm and 398 nm). Figure 9 shows the emission spectra of the chitosan compound with Eu^{3+} ion in the powder form. The emission spectra in these wavelengths show a broad band related to chitosan transitions, given that the compound is being excited in its excitation region, as previously analyzed. The peaks related to transitions $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ in the Eu^{3+} ion appear at 580 nm, 593 nm, 616 nm, 646 nm and 682 nm, respectively. Because the $^5D_0 \rightarrow {}^7F_2$ transition has greater intensity and is more influenced by the ligand field, it is considered hypersensitive, exhibiting red emission. It is also suggested, in this case, that chitosan is not transferring energy to the lanthanide ion; however, the chemical environment where the lanthanide

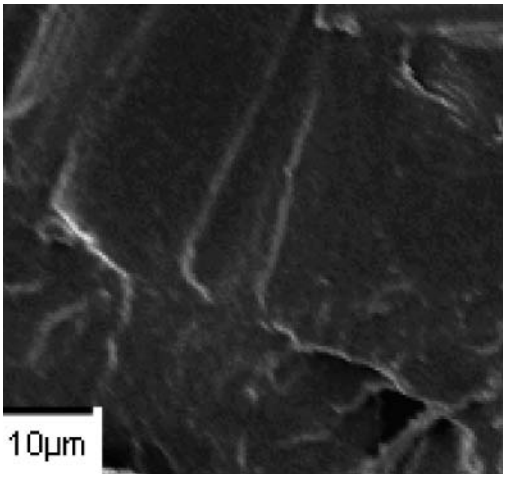

Fig. 10. SEM result for pure chitosan membrane, showing the cross section, with magnification of 1×10^3.

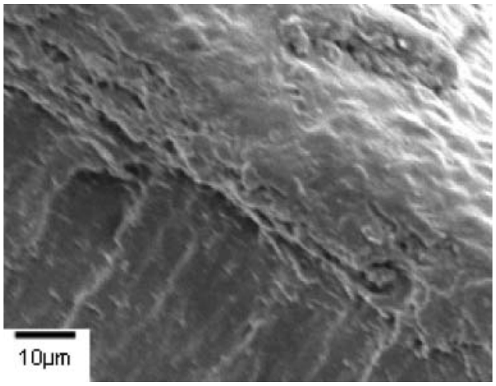

Fig. 11. SEM result for chitosan with Eu^{3+} ion membrane, showing the cross section, with magnification of 1×10^3.

ions are found breaks the selection rules and favors the Eu^{3+} emission.

3.4.4. *Scanning electron microscopy (SEM)*

Figure 10 shows the cross section image for chitosan, with magnification of 1×10^3. It is observed on this micrograph a dense aspect throughout the pure chitosan membrane. Figure 11 shows cross-sectional image of chitosan membrane with the Eu^{3+} ion, with magnification of 1×10^3. It can be observed that the membrane is not uniform, indicating that the Eu^{3+} ion is coordinated in the structure of chitosan.

4 Conclusions

TG/DTG curve of pure chitosan membrane showed two stages of weight loss, whereas chitosan powder had three stages of weight loss. The third stage of the TG/DTG curves indicates that the lanthanide ions cause gradual degradation of the residual carbons. The SEM results of chitosan membrane with Eu^{3+} ion suggested that the metal ion is bound to chitosan. It is suggested that chitosan is not transferring energy to the lanthanide ions, however, the chemical environment in which the lanthanide ions were found breaks the selection rules and favors both Eu^{3+} and Tb^{3+} emission. Charge transfer bands were also observed. The 4f-4f transitions from the fundamental to the excited state of the Eu^{3+} and Tb^{3+} ions were observed; these are more commonly found in vitreous systems. Because the compounds of chitosan with Eu^{3+} (membrane form) and the chitosan with Eu^{3+} and Tb^{3+} ions (powder form) have relatively high emissions in the visible region, they could be promising as luminescent probes in biochemical systems.

Acknowledgments

We would like to thank S. Alves Jr. from the Department of Fundamental Chemistry at the Universidade Federal de Pernambuco (UFPE) for the luminescence measurements. Financial support by CAPES is also gratefully acknowledged.

References

1. Peniche, C., Waldo A.M., Natalia D., Roberto S., Roberto A. G. and Julio S.R. (1999) *Biomaterials*, 20, 1869–1878.
2. Odilio, B.G. and Valmir, L. (2003) *Polímeros: Ciência e Tecnologia*, 13, 223–228.
3. Dung, P.L., Milas, M., Rinaudo M. and Desbrières, J. (1994) *Carbohydrate Polymer*, 24, 209–214.
4. Wang, K., Rongchang, L., Yi, C. and Bing, Z., Lanthanides—the future drugs? (1999) *Coordination Chemistry Reviews.*, 190–192, 297–308.
5. Guibal, E. (2004) Separation and Purification Technology., 38, 43–74.
6. Wang, A., Zhao, P., Gao, X. and Yu, X. (1999) *Spectroscopy and Spectral Analysis*, 19, 819–820.
7. Ozaki, T., Yoshida, Z., Nankawa T., Yoshida, T., Ohnuki, T. and Francis, A.J. (2006) *Journal of Alloys and Compounds*, 408–412, 1334–1338.
8. Chun,Y., Si-Dong, L., Cheng-Peng, L., Chao-Hua, Z., Lei,Y. and Chong-Peng, C. (2008) *Journal of Applied Polymer Science*, 109, 957–962.
9. Jiang, H., Liang, J., Grant, J.T., Su, W.T., Bunnins, J., Cooper, T.M. and Adams, W.W. (1997) *Macromolecular Chemistry and Physics*, 198, 1561–1578.
10. Wang, A., Shao, S., Zhou, J. and Yu, X. (2000) *Acta Polymerica Sinica*, 193, 299–300.
11. Rhazi, M., Desbières, J., Tolaimate, A., Rinaudo, M., Vottero, P., Alagui, A. and El Meray, M. (2002) *European Polymer Journal*, 38, 1523–1530.
12. Ozaki, T., Kimura, T., Yoshida, Z. and Francis A.J. (2003) *Chemistry Letters*, 32, 560–561.
13. Malta, O.L., Legendziewicz, J., Huskowska, E., Turowska-Tyrk, I., Albuquerque, R.Q., Donega, C.M. and Silva F.R.G. (2001) *Journal of Alloys and Compounds*, 323–324, 654–660.
14. Blasse, G. and Grabmaier, B.C. (1994) *Luminescent Materials*, 130, 123–127.
15. Alexandre, T.P., Marcos, R.G., Adriano, V.R., Elias, B.T., Jorge, N. and Edvani, C.M. (2007) *Journal Hazardous Materials*, 58, 652–659.
16. Tao, Y., Pan, J., Yan, S., Tang, B. and Zhu, L. (2007) *Material Science and Engineering B*, 138, 84–89.
17. Xue-Yin, J., Yan, J., Zhi-lin, Z. and Shao-hong, X. (1998) *Journal of Crystal Growth*, 191, 692–696.
18. Malta, O.L. and Silva. F.R.G. (1995) *Spectrochimica Acta Part A — Molecular and Biomolecular Spectroscopy.*, 54, 1593–1599.
19. Lakshminarayana, G. and Buddhudu, S. (2007) *Materials Chemistry and Physics*, 102, 181–186.
20. Carnall, W.T., Goodman, G.L., Rajnak, K. and Rana, R.S. (1989) *Journal Chemical Physics.*, 90, 3443–3457.
21. Wang, F., Zhang, Y., Fan, X. and Wang, M. (2006) *Nanotechnology*, 17, 1527–1532.