

Microarticle

Study on the degradation of chitosan slurries

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ABSTRACT

In the present work, we measured the degradation rate of different chitosan slurries. Several parameters were monitored such as temperature (25 °C, 37 °C, 50 °C); chitosan concentration (1% and 2% (w/V)); and polymer molecular weight. The samples were tested in dynamic sweep test mode. This test is able to provide a reliable estimation of viscosity variations of the slurries; in turn, these variations could be related to degradation rate of the system in the considered conditions. The resulting information is particularly important especially in applications in which there is a close relationship between physical properties and molecular structure.

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Introduction

Among natural biocompatible polymers, chitosan (CS) is considered as a *gold standard*, as it presents several bio-relevant properties: in particular, it is nontoxic, biodegradable and easily bioabsorbable [1–3]. In addition to this, it also possesses the capability to create gel-like structures at different pH values [4]. In terms of rheological characterization, CS exhibits a typical non-Newtonian behavior, which is strictly related with the degree of deacetylation. This characteristic has been attributed to the expanded structure and to the increase of entanglements between the chains [5]. Several previous studies have reported chitosan thermal decomposition due to hydrolytic depolymerization [6]. Moreover, this mechanism is strongly influenced by the pH and molecular weight of the polymer chains [7].

On such bases, in this work, we measured the degradation rate of different chitosan slurries. Different parameters were monitored such as temperature (25 °C, 37 °C, 50 °C); chitosan concentration (1% and 2% (w/V)); and polymer molecular weight. The samples were tested in dynamic sweep test mode: this procedure provides a reliable estimation of viscosity variations of the slurries; in turn, these variations could be related to degradation rate of the system in the considered conditions [8–15].

Material and methods

The slurries were produced with three different CS products purchased from Sigma Aldrich: medium molecular weight (mMW), high molecular weight (hMW), and low molecular weight (lMW). The chitosan solution was prepared in a stock of 100 ml. To allow a more robust comparison of results, all the samples were obtained starting from the same solution. Briefly, the required volume of water was measured, then the required 0.1 M acetic acid was poured in, and the weighted CS was added in a glass flask to obtain concentration of 1% and 2% (w/V). The resulting pH condition (i.e., pH ≈ 4) enables CS solvation and the achievement of a homogenous solution (in ≈1 h) by protonation of the NH₂ amino groups. The flask was sealed to avoid evaporation of water, and to maintain the concentration of the solution. The obtained solution was stored at 4 °C before using it, so as to avoid uncontrolled degradation. Slurries with different chitosan MWs and concentrations were tested in a dynamic controlled mode with a rotational rheometer (Kinexus PRO+, Malvern, UK). Additionally, slurries with the same composition were exposed to different temperatures to gather information about the influence of temperature on the degradation rate. For the experiments, cone and plate geometry with 40 mm diameter and a 1 mm-thick gap was used. The measurement program was a viscometry single-rate test with a shear rate of 1.0 s⁻¹ at 25 °C to measure the dynamic viscosity (η). The percentage dynamic viscosity, $\eta_{\%}$, was obtained through the following equation:

$$\eta_{\%} = \eta_0 / \eta_x \quad (1)$$

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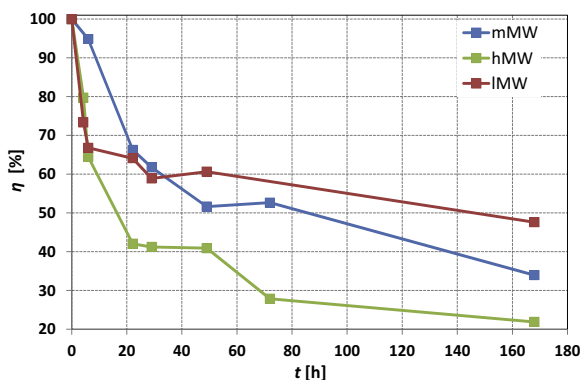


Fig. 1. Percentage dynamic viscosity ($\eta\%$) as a function of time, for different chitosan slurries with 1%CS, after thermal treatment at 37 °C.

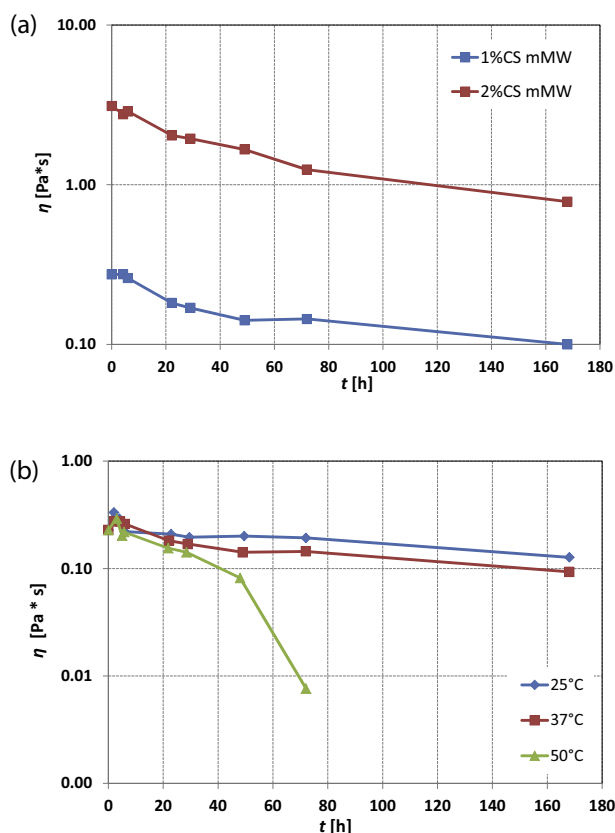


Fig. 2. (a) Dynamic viscosity (η) as a function of time, for 1% and 2% CS solutions with mMW chitosan after thermal treatment at 37 °C (b) Dynamic viscosity (η) as a function of time, for different chitosan solution with 1% mMW CS with different exposed temperatures (25 °C, 37 °C and 50 °C).

where η_0 is the initial viscosity (at instant $t = 0$), and η_x is the viscosity at the generic instant $t = x$.

To assess the influence of CS concentration on the viscosity, measurements were performed on samples with two different CS concentrations (namely, 1% and 2% (w/V)) using mMW chitosan.

Furthermore, degradation tests of the CS slurries were performed at three different temperatures (i.e., 25 °C, 37 °C, 50 °C) with a solution of the composition 1% CS and mMW.

Experimental results

Fig. 1 shows the behavior of the dynamic viscosity ($\eta\%$) over time, for different chitosan slurries: it can be seen that, for all

the considered slurries, the value of $\eta\%$ decreases over time. This behavior is to be attributed to the thermal treatment at 37 °C in an acidic environment, which leads to the depolymerization of chitosan, as reported in [16]. In fact, as a consequence of the depolymerization, the MW decreases and thereby the viscosity of the solution.

Fig. 1 also shows the different degradation rates in dependence on the MW of the polymer; in particular, a higher MW of chitosan results in an increased degradation rate.

Fig. 2 shows the behavior of the dynamic viscosity, η , as a function of time. By increasing the chitosan concentration from 1% CS to 2% CS, the value of η increases by a factor greater than 10. Since the solubility and the homogeneity of the reaction mixtures depend on the viscosity, a suitable polymer concentration must be used. For this reason, the minimum level of CS concentration was fixed at 1%, as reported in [17].

To study the influence of temperature on the degradation rate, a chitosan solution with the composition of 1% mMW CS was exposed to three different temperatures (25 °C, 37 °C and 50 °C). Fig. 2 shows the dynamic viscosity (η) as a function of time: it can be seen that only the sample treated at 50 °C exhibits a decrease of dynamic viscosity over time. This behavior is caused by the acidic induced degradation of the glycosidic bonds of the chitosan; in other words, the depolymerization of the chitosan is increased when the activation energy threshold is achieved. Conversely, at 25 °C and at 37 °C, no significant variation of the degradation rate is observed over time.

Conclusions

This study demonstrated a clear dependence of the degradation rate of CS slurries on different parameters, namely chitosan MWs, concentration and temperature. In particular, a considerable effect was observed when the temperature was raised up to 50 °C. This particular condition was able to reduce the viscosity values by two orders of magnitude after 72 h. As for the 37 °C condition, in this case, the degradation rate variation over time was barely affected. This suggests the existence of a sort of cut-off temperature value (between 37 °C and 50 °C), for which the elapsed time (t) starts to have a dramatic effect on the degradation rate. The effect of chitosan MW was relevant for all the tested samples, but the negative effect was observed for the hMW sample.

Overall, the obtained results demonstrate that there is a direct relationship between solvating conditions and chitosan backbone integrity over time in acidic environment. This, in turn, indicates that it is to pay attention to all those conditions during the preparation of CS-based devices.

References

- [1] Carraher C, Seymour R. *Polymer chemistry*. CRC Press; 2007.
- [2] Ferdous J et al. *Acta Biomater* 2013;9:6052–61.
- [3] Di Mario F et al. *Int J Biol Macromol* 2008;43:8–12.
- [4] Roberts G. *Chitin chemistry*. Macmillan; 1992.
- [5] Wang W, Xu D. *Int J Biol Macromol* 1994;16:149–52.
- [6] BeMiller J. *Adv Carbohydr Chem Biochem* 1966;22:25–108.
- [7] Dimida S et al. *J Appl Polym Sci* 2015;132:42256.
- [8] Madaghiele M et al. *J Appl Biomater Funct Mater* 2014;12:183–92.
- [9] Cannazza G et al. *Water* 2014;6:2056–69.
- [10] Demitri C et al. *Interface Focus* 2014;4:20130053.
- [11] Raucci M et al. *J Appl Biomater Funct Mater* 2012;10:302–7.
- [12] Sannino A et al. *J Appl Polym Sci* 2010;115:1438–44.
- [13] Demitri C et al. *Measurement* 2016;90:418–23.
- [14] Demitri C et al. *J Biomed Mater Res – Part A* 2016;104:726–33.
- [15] Raucci M et al. *J Biomed Mater Res – Part A* 2015;103:2045–56.
- [16] De Benedictis V et al. *Polymers* 2016;8:210.
- [17] Demitri C et al. *Polymers* 2015;7:2584–94.