

Thermal Stability and Kinetics of Sodium Alginate and Lignosulphonic Acid Blends

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Abstract: Biodegradable polymer blends are prepared by mixing two natural biodegradable polymers Sodium alginate (SA) and Lignosulphonic acid (LS) by solution casting method for controlled drug delivery application. Successful application of blend for controlled drug delivery requires its stability under physiological condition. Thermal analysis (TGA) reveal thermal transitions, degradation processes and thermal stability of blends and gives an important insight about its stability. In this paper TGA data has been used to evaluate degradation of SA/LS blends with temperature. The energy of activation for the thermal degradation of polymers and blends has been calculated by 'Horowitz and Metzger' method. These studies reveal that blends are stable as compared to their polymers.

Keywords: Sodium alginate, Lignosulphonic acid, Polymer blends, Thermal stability

1. INTRODUCTION

Biopolymers are used extensively for wound enclosures, body implants, tissue engineering materials, drug delivery matrices or vehicles, dental applications, diagnostics and therapeutic imaging [1]. These polymers are biocompatible, biodegradable and can be obtained universally. Biopolymers, in their original form may lack in certain features necessary for a particular application. In order to improve properties, and make them suitable for application, they are usually blended with another polymer. Blending of existing polymers can often be achieved rapidly than creating entirely new polymers. The study of polymer's properties, their interaction and resulting features when blended is an important area of study.

Sodium Alginate (SA), a biopolymer obtained from brown sea weed, is extensively used in medicine for wound dressing, cell and enzyme immobilization, controlled drug delivery etc [2]. Its polymeric chain consists of β -D-mannuronic acid (M) and its C-5 epimer α -L-guluronic acid (G) monomers, which are linked by 1-4 glycosidic linkages. The structure and properties of alginates depends on the G:M ratio, but in general they are biodegradable, non-toxic, biocompatible and have the ability to form hydrogels under mild conditions [3]. Alginate hydrogels are employed for drug

release applications. These hydrogels show poor mechanical stability under physiological conditions [4-5] which is improved by adding suitable polymer/additive as filler. Some of the blends of SA prepared by solvent casting method are listed in Table 1. Aloe Vera gel, known for therapeutic properties was blended with SA by solvent casting method by Ruben Piera et al [6]. Synthesized blend films showed better thermal and mechanical properties than SA and the Film showed stability in simulated body fluid condition. Aloe Vera quantity was found to control the stability and degradation of blend film.

A better water vapor permeability, swelling capacity, thermal stability and tensile strength was achieved by blending SA with Silk fibroin [7]. SEM and XRD of the blend revealed microscopic phase separation and amorphous nature respectively. Chitosan is extensively used in food and medicine for its diverse properties. Blend films with chitosan also showed better thermal and mechanical stability as compared to SA [8]. In order to combine the properties of both chitosan and sodium alginate a blend with medical clay, montmorillonite (MMT) was prepared by solvent casting method also showed improvement in properties and diffusion and swelling controlled drug release [9]. A stable, pH dependent controlled drug release material was achieved by blending Guar gum, sodium alginate and

Table 1. List of Sodium alginate (SA) blends

Sl.No	SA Blends	Scope of Study	Ref No.
1.	SA and Aloe Vera	Wound healing and drug delivery applications	6
2.	SA and silk fibroin (SF)	Wound healing	7
3.	SA and Chitosan	Improvement in properties	8
4.	SA, Chitosan and Montmorillonite	Drug delivery	9
5.	SA and Guar gum and with Cloisite 30B	Drug delivery	10
6.	SA and Chitosan	Drug delivery	11
7.	SA and Collagen	Food Packaging	12
8.	SA and Poly ethylene glycol(PEG)	Improvement in properties	13
9.	SA and Poly ethylene oxide(PEO)	Improvement in properties	14

Cloisite 30B [10]. In another study viscous and macroscopically homogeneous SA chitosan hydrogel structures were developed by Dominika Kulig et al [11]. The blend showed improvement in thermal, chemical and mechanical properties and stability as compared to SA. TGA analysis showed that thermal decomposition of blend improved by increasing chitosan dosage. In case of SA/collagen, blend films with improved viscosity, thermal stability and mechanical property as compared to pristine polymers was achieved. [12]. Formation of thermally stable and immiscible blend of SA with Poly ethylene glycol was reported by Mruthyunjaya swamy and Ramraj [13]. Poly ethylene oxide (PEO)/ Sodium Alginate (SA) blends showed effect of SA quantity on their thermal degradation temperatures. The thermal behavior of blend was attributed to the hydrogen bond formed between the ether oxygen of PEO and the hydroxyl groups of SA [14].

Inspired by the volumes of literature available on sodium alginate blends and the need for better controlled drug release vehicles, we blended SA with sodium lignosulphonate (LS), a biopolymer from plant source [15]. LS is often used as super plasticizer. The SA/LS blend prepared in 80/20 ratio was found to be most suitable for controlled release of drug Ciprofloxacin under intestinal condition [16]. We have reported in our previous publications

from the XRD and FTIR that the SA/LS blends have shown improved crystallinity while the polymers retained their structure in the blend [17]. Thermal studies are important tool to investigate a material for its suitability as drug delivery vehicle. Polymeric materials with glass transition temperature more than body temperature (37 °C) are stable under aqueous condition and thus are suitable for drug release applications [18]. A material used for controlled release is expected to be stable for longer period of time in aqueous medium in order to retain the drug in its matrix and release the drug systematically in a controlled manner [19]. The knowledge of thermal stability and kinetic parameters of thermal degradation process of polymers and their blends are important in the processing of polymeric material for drug release applications. In the present work, we have investigated the kinetics of thermal degradation of the prepared blends of SA with LS to reveal the effect of blend ratio on thermal stability.

2. EXPERIMENTAL

2.1. Chemicals

Both SA and LS of analytical grade are purchased from Sigma-Aldrich, India Limited

and used without any further purification. Solutions of polymers have been prepared in distilled water.

2. 2. Preparation of SA / LS Blends

SA of desired weight has been soaked in double distilled water for 24 hours prior to mixing. In order to prepare blends of varying composition aqueous solution of thus prepared SA was mixed with aqueous solution of LS in the ratio 100/0, 80/20 and 60/40 by weight and the mixture was continuously stirred for 30 mins using magnetic stirrer. Thin films of different compositions were casted by pouring the resultant mixture on glass substrates, dried at room temperature for 72 h, and then dried at 60 °C in a vacuum oven till constant weight is achieved [20].

2. 3. Characterization Techniques

The SA, LS and their blends samples were subjected for TGA in order to investigate the initial and final degradation temperature. The TGA was performed on a TA instrument “Universal V4.7 TA”. The sample tests were conducted in an N₂ purge over a temperature range of 20–600 °C at a scan rate of 10 °C/min[21].

3. RESULTS AND DISCUSSIONS

In a heating process, a material loses moisture attached to its surface, water entrapped within and decomposes due to breaking of its bonds. It is well established that blending may greatly influence the thermal stability of the component polymers [22–24]. During the process of degradation, considerable interactions may occur between components in the blend and/or their degradation products. The type of interaction depends on the degree of miscibility of the components, nature of the compositions and their ratio in the blend. In general, the first heating stage of polymers due to loss of water show a small (5–15%) mass loss while the second decomposition step show significant mass loss (39–75%). The delay in this process is indicative of stability of a material. Thermal degradation process (TGA) of a material is studied by observing mass loss of a sample as a function of time or temperature in a varied and controlled atmosphere.

The weight loss (TGA) and derivative of weight loss (DTG) curves of pure SA, pure LS and SA/LS blends in ratio 80/20 and 60/40 are presented in Fig. 1 and Fig. 2 respectively. SA in

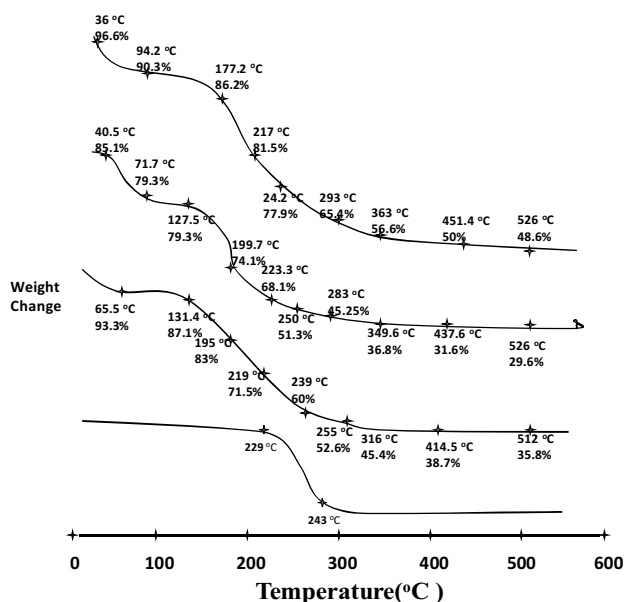


Fig. 1. TGA curves of a) Pure SA b) SA/LS (80/20) c) SA/LS (60/40) and d) Pure LS

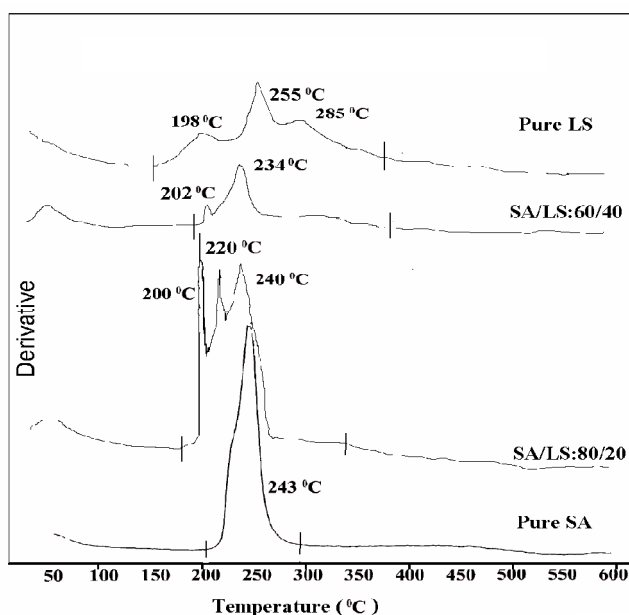


Fig. 2. Derivative of TGA curves of a) Pure SA b) SA/LS (80/20) c) SA/LS (60/40) and d) Pure LS

N₂ atmosphere degrades in two stages - The initial step is due to loss of water attached and the final due to decarboxylation reaction of alginate, fracture of glycosidic bonds, and dehydration and decarboxylation of alginate [21, 25]. Pure LS on the other hand degrades in multiple steps. Its initial mass loss due to water evaporation is observed at relatively lower temperature. Further degradation process is slow and observed over a range of temperature involving chain degradation [26]. TGA and DTG of blends on the other hand show that addition of LS improves thermal stability of SA. The SA/LS (80/20) blend shows degradation over a range of temperature. A lower concentration of LS is expected to reduce

existing intermolecular forces in SA polymeric chains thereby improving the flexibility and chain mobility. The TGA of SA/LS (60/40) blend shows rapid mass loss in the second stage as compared to SA/LS (80/20). This is an indicative of reduced stability due to phase separation. Stability of blends is also reflected by studying the residual mass at 300 °C, 400 °C and 500 °C temperatures [Table 2]. SA/LS (80/20) blends shows a delay in mass loss as compared to the pure SA and the SA/LS (60/40) blend. It can be concluded that the increased mass ratio of LS (40%) exceeds the compatibility limit of SA thus making the blend unstable. This blend has also shown a fast degradation under aqueous condition [16].

Table 2. Degradation temperatures of SA, LS and their blends

Polymer	IDT	Wt. loss (%) 300 °C	Wt. loss (%) 400 °C	Residue (%) 500 °C
Pure SA	200 °C	61.2	68.72	28.38
SA/LS(80/20)	195 °C	51.78	60.68	36.3
SA/LS(60/40)	199 °C	58.39	68	29.8
Pure LS	177 °C	37.9	47.7	49.39

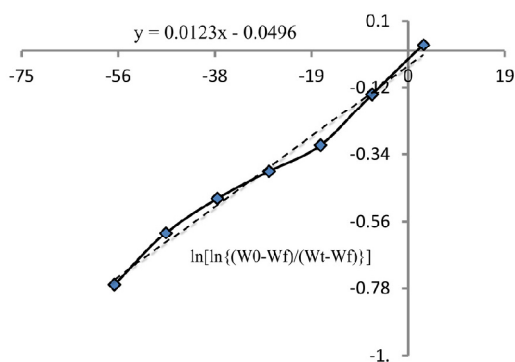


Fig. 3. Calculation of Energy of Activation for pure SA

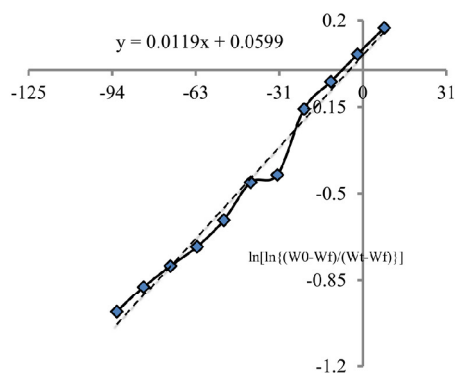


Fig. 4. Calculation of Energy of Activation for blend SA/LS (80/20).

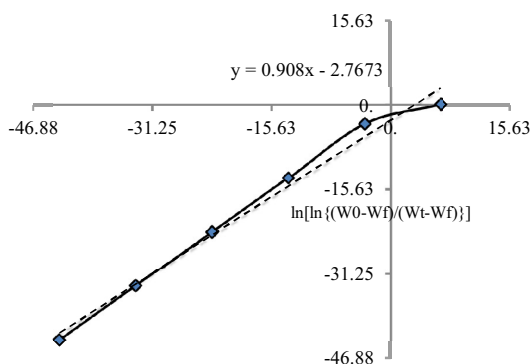


Fig. 5. Calculation of Energy of Activation for blend SA/LS (60/40).

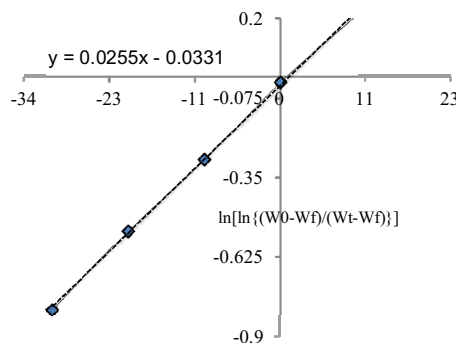


Fig. 6. Calculation of Energy of Activation for pure LS

The thermal data also indicate that the blend formation improves the stability but does not cause change in polymer degradation mechanism. It is clear that the degradation is delayed as the blend has better alternative ways like increase in interfacial area, diffusion of chains among the phases to dissipate the accumulated energy during the heating process. These alternative pathways for the dissipation of the energy increase the thermal stability of polymers [27]. In order to understand the degradation process, energy of activation (E_a) for the thermal degradation of pure SA, LS and their blends in the regions 200 °C to 250 °C has been estimated using 'Horowitz and Metzger' method [28]. According to this method a plot of double logarithm of the reciprocal of the reactant versus temperature gives the energy of activation of pyrolysis. For first order kinetics the equation is:

$$\ln[\ln \{(W_0 - W_f) / (W_t - W_f)\}] = E_a \Theta / RT_s^2 \quad (1)$$

where W_0 = initial weight of the sample

W_f = final weight of the sample

W_t = the weight of the sample at temperature 't'.

R = gas constant

$\Theta = T - T_s$, T_s is the reference temperature when $(W_t - W_f) / (W_0 - W_f) = 1/e$

A plot of double logarithm of the reciprocal of the weight fraction of the reactant versus temperature whose slope ($E_a \times 10^3$) is related to energy of activation.

Fig. 3 to Fig. 6 show the plots obtained from kinetic analysis of TGA data of pure SA, pure LS and their blends SA/LS (80/20) and SA/LS (60/40). The energy of activation is calculated from these plots and results are presented in

Table 3. Energy of Activation of pure SA, LS and their blends (SA/LS)

Samples	Energy of activation (kJ/mol)
Pure SA	6.754
SA/LS(80/20)	8.435
SA/LS(60/40)	9.261
Pure LS	12.21

Table 3. Energy of activation for pure SA is 6.754 kJ/mol and on blending with LS in the ratio SA/LS (80/20) and SA/LS (60/40) the energy of activation increased to 8.435 and 9.2614 kJ/mol. The increase in E_a confirms that addition of LS improves the thermal stability of SA.

4. CONCLUSION

TGA and derivative TGA data show that the stability of SA has been enhanced by addition of LS. Study also indicate that the blends are immiscible. Immiscibility leading to two or multiple phases during blending is required in many applications. In case of immiscible blends each phase contributes its own characteristics to the blend material which is a required attribute in some applications. The TGA curves indicate that, SA/LS blends degrade in multiple steps as shown by a multiple peaks. The kinetic studies of SA/LS blends using 'Horowitz and Metzger' method shows better thermal stability than their polymers. The composition 80/20 exhibits better thermal stability as well as the energy of activation thus calculated. It is an established fact that the stability of blends influence the release of drug from polymer matrix and hence the SA/LS blend (80/20) can show better drug release ability and thus have potential applications as controlled drug delivery system.

REFERENCES

1. Michael Niaounakis., Biopolymers: Applications and Trends, ISBN: 978-0-323-35399.
2. Vignesh, S., Aswathi Gopalakrishnan., Poorna, M. R., Shantikumar. V. Nair, Jayakumar, R., Ullas Mony., "Fabrication of micropatterned alginate-gelatin and k-carrageenan hydrogels of defined shapes using simple wax mould method as a platform for stem cell/induced Pluripotent Stem Cells (iPSC) culture". Int J Biol Macromol., 2018,112, 737-744.
3. Shilpa, A. Agrawal, S. S., and Ray, A. R., "Controlled delivery of drugs from alginate matrix". Polym. Rev., 2003, 43, 187-190.
4. Kalyani, S., Smitha., Sridhar, S. and Krishnaiah, A., "Pervaporation separation of ethanol-water mixtures through sodium alginate membranes." Desalination, 2008, 229, 68-71.
5. Riyajan, S. A. and Tangboriboonrat, P., "Encapsulation of Carbendazim with Epoxidized Natural Rubber/Sodium Alginate." Polymer (Korea)., 2015, 39, 550-555.
6. Rúben, F. Pereira., Anabela Carvalho., Gil, M. H., Ausenda Mendes., Paulo J. Bártolo., "Influence of Aloe vera on water absorption and enzymatic in vitro degradation of alginate hydrogel films", Carbohydrate Polymers., 2013, 98, 311– 320.
7. de Moraes, M. A., Silva, M. F., Weska, R. F., Beppu, M. M., "Silk fibroin and sodium alginate blend: miscibility and physical characteristics", Mater Sci Eng C Mater Biol Appl, 2014, 40, 85-91.
8. Xia, W., Liu, P., Zhang, J. and Chen, J., "Biological activities of chitosan and chitooligosaccharides". Food Hydrocoll., 2011, 25, 170–179.
9. Nayak, P. L., Debasish Sahoo., "Chitosan-alginate composites blended with Cloisite 30B as a novel drug delivery system for anticancer drug paclitaxel". International Journal of Plastics Technology., 2011, 15(1), 68-81.
10. Rajashree Chahatray., Sahoo,D., Mohanty,D.P and Nayak, P. L., "Guargum-Sodium Alginate Blended with Cloisite 30B for Controlled Release of Anticancer Drug Curcumin", World Journal of Nano Science & Technology., 2013, 2(1), 26-32.
11. Dominika Kulig., Anna Zimoch-Korzycka., Andrzej Jarmoluk., Krzysztof Marycz., "Study on Alginate-Chitosan Complex Formed with Different Polymers Ratio". Polymers., 2016, 8(5), 167-170.

12. Zhe Wang., Shuaifeng Hu., and Huaiyu Wang., "Scale-Up Preparation and Characterization of Collagen/Sodium Alginate Blend Films". *Journal of Food Quality.*, 2017, 12, 42–50.
13. Mruthunjaya swamy, B. and Ramraj., "Sodium alginate and poly (ethylene glycol) blends: Thermal and morphological behaviors". *Journal of Macromolecular Science -Part A.*, 2010, 47(9), 877.
14. Tuncer Çaykara., Serkan Demirci., S. Mehmet and Eroğlu., Olgun Güven., "Poly(ethylene oxide) and its blends with sodium alginate", *Polymer.*, 2005, 46(2), 10750-10757.
15. Giridhar Reddy, S. and Akanksha Saxena Pandit., "Swelling Behavior of Calcium-ions Cross-linked Bipolymeric Sodium Alginate–Lignosulphonic acid blends". *Int Jou of Polym Mat.*, 2011, 60, 1123-1129.
16. Giridhar Reddy, S. and Akanksha Saxena Pandit., "Controlled drug delivery studies of biological macromolecules: Sodium alginate and Lignosulphonic acid film". *Journal of Applied Polymer Science.*, 2014, 131, 40442.
17. Giridhar Reddy, S. and Akanksha Saxena Pandit., "Biodegradable Sodium alginate and Lignosulphonic acid Blends: Characterization and Swelling Studies". *Polimeros.*, 2013, 23(1), 13-18.
18. Rao, K. V. R. and Devi, K. P., "Swelling controlled-release systems: recent developments and applications". *International Journal of Pharmaceutics.*, 1988, 48, 1-5.
19. Y.W. Chien, Concepts and system design for rate-controlled drug delivery, in: Y.W. Chien (Ed.), *Novel Drug Delivery Systems*, Marcel Decker, Inc; New York, (1992), 1-42.
20. Katzhendler, I., Hoffman, A., Goldberber, A. and Friedman, M., "Modeling of drug release from erodible tablets". *Journal of Pharm Sciences.*, 1997, 86, 110-115.
21. Soares, J. P., Santos, J. E., Chierice, G. O and Cavalheiro, E. T. G., "Thermal behavior of alginic acid and its sodium salt". *Ecl. Quím.*, 2004, 29(2), 53-56.
22. Goh, S. H., "Thermogravimetric study of the thermal stability of poly(vinyl chloride) / poly (vinyl acetate) blends". *Thermochim Acta.*, 1993, 215, 291-295.
23. Klarić, I., Roje, U and Stipanelov, N., "Kinetic investigation of thermooxidative degradation of poly(vinyl chloride)/acrylonitrile–butadiene–styrene blends by isothermal thermogravimetric analysis". *J. Appl. Polym. Sci.*, 1999, 71, 833-838.
24. McNeill, I. C., "Thermal degradation mechanisms of some addition polymers and copolymers". *J. Anal. Appl. Pyrolysis*, 1997, 21, 40-41.
25. Yun Liua., Jin-Chao Zhaoa., Chuan-Jie Zhang., Yi Guo, Li Cuia., Ping Zhu and De-Yi Wang., "Bio-based nickel alginate and copper alginate films with excellent flame retardancy: preparation, flammability and thermal degradation behavior". *RCS Advances.*, 2015, 64125-64137.
26. Emma Jakab., Oskar Faixb., Ferenc Tilla and Tamás Székely., "The effect of cations on the thermal decomposition of lignins". *Journal of Analytical and Applied Pyrolysis.*, 1993, 25, 185-194.
27. Rafael Silva., Gizilene, M., Edvani, C., Muniz., Adley, F and Rubira., "Miscibility Influence in the Thermal Stability and Kinetic Parameters of Poly (3-hydroxybutyrate)/ Poly (ethylene terephthalate) Sulphonated Blends". *Polímeros.*, 2010, 20(2), 153-158.
28. Horowitz and Metzger., "A New Analysis of Thermogravimetric Traces". *Anal. Chem.*, 1963, 35(10), 1464-1468.