ISGC 2022

N°152 / OC
TOPIC(s) : Polymers or composites / Waste and side streams valorization

Effect and Stability of Green Additives on Chitosan-Based Bioplastic Films

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PURPOSE OF THE ABSTRACT

With our steadily growing demand in energy and chemicals [1], a wide variety of different technologies is needed to evolve in two ways. Firstly, already abundant resources need to be valorised and recycled to avoid the production of waste [2]. Secondly, alternative and renewable resources like natural polymers need to be identified to gradually reduce the dependence on exhaustible fossil fuels [1,3]. The non-toxic properties of natural polymers as well as their biodegradability are often advantageous over their counterparts derived from petrochemicals [3]. In particular, chitin-derived chitosan is highly abundant in e.g. shrimps and crabs and arises as waste product from the food industry, which is biodegradable [4]. It shows a strong backbone structure, which makes it a potentially highly valuable material for industrial application. As chitosan alone is limited in solubility and stability, seven biodegradable additives are investigated in this work to optimize properties such as strength, flexibility, and elasticity, to create suitable alternatives for fossil-based plastics [5].

We have discovered that mixing chitosan with the chosen additives resulted in formable films, with properties already distinguishable by eye (Figure 1). The films, and later crab shapes, were prepared by dissolving chitosan powder in 1wt% acetic acid/water solution for 24 h, which was subsequently drop casted and dried at room temperature. The pure chitosan film and the films formed with addition of sorbitol (SOR), glycerol (GLY) and polyethylene glycol (PEG) show incorporation of air bubbles (Figure 1, left). This was not observed with citric acid (CA), lactic acid (LAC), Tween 20 (T20) and Tween 80 (T80) (Figure 1, right). Furthermore, addition of GLY resulted in a very soft and flexible film, while the film formed with PEG was hard and brittle. With T20 and T80, the film was strengthened substantially but also assumed a white sheen. Flexibility was achieved by adding SOR, but this additive did not induce much strength, while LAC and CA strengthened the film and additionally increased flexibility. These by-eye investigations were further examined by quantitative nanomechanical mapping (QNM).

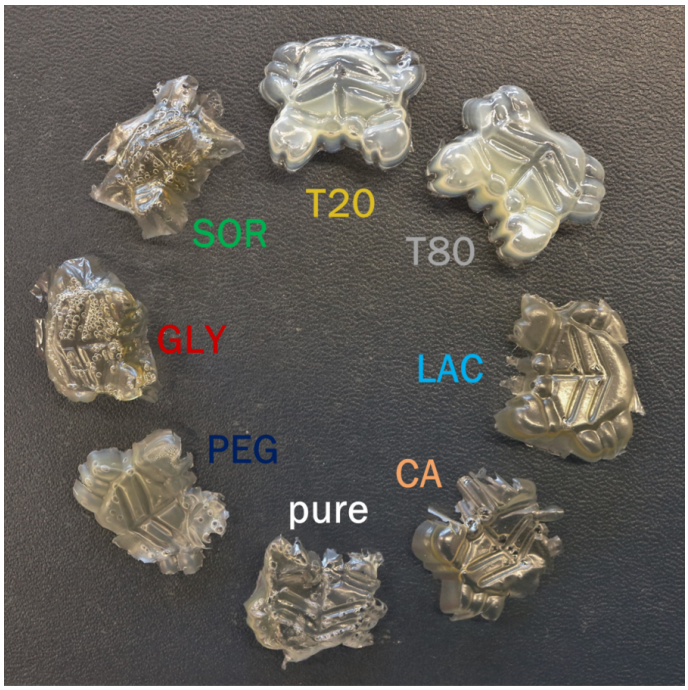
Furthermore, the effective incorporation of additives with varying the additive to chitosan ratios of 0.5:1 up to 8:1 as well as the effect on crystallinity and crosslinking were investigated by infrared spectroscopy (Figure 2), pyrolysis pyrolysis gas chromatography coupled with mass spectrometry (py-GC-MS), and X-ray diffraction (XRD). The additives could be categorized in three groups, namely non-saturating plasticizer (Figure 2a and d; GLY and PEG), saturating plasticizer (Figure 2b and e; SOR, T20, and T80), and crosslinking plasticizers (Figure 2c and f, LAC and CA).

IR and py-GC-MS showed that for the saturating plasticizers an uptake maximum was reached at a ratio of approximately 1:4, while non-saturating plasticizers were fully incorporated into chitosan. For additives with multiple functionalities py-GC-MS fragmentation patterns indicated a crosslink formed between chitosan even at room temperature, also visible from the shift of the N-H bend at 1560 cm-1 in the IR spectra.

Additionally, py-GC-MS data and GI-XRD data showed a reacetylation of chitosan resulting in a stronger material. This was only observed for the pure chitosan film, with CA as well as with LAC, but not with other additives. This indicates that all the other non-crosslinking additives compete with acetic acid and prevent acetic acid from re-acetylating chitosan.

With the additives investigated, it would be possible to utilize a highly abundant natural raw material in sustainable packaging materials, providing an alternative to diminishing fossil fuel-based versions. Especially LAC and CA showe promising results for future application. This research shows that a very broad range of properties can be achieved by adding the investigated additives with this easy synthesis method.

FIGURES



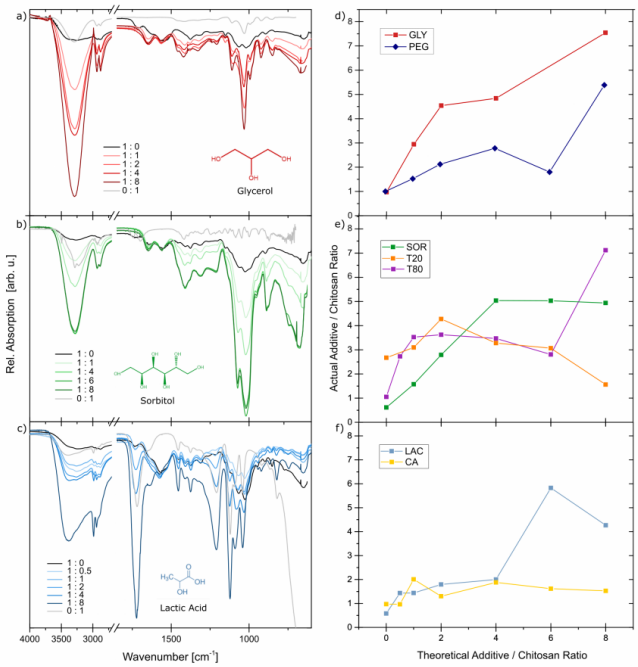


FIGURE 1

Figure 1.

Crabs made from 1:1 solutions of chitosan with the additives polytheyleneglycol (PEG; non-saturating), glycerol (GLY; non-saturating), sorbitol (SOR; saturating), tween 20 (T20; saturating), tween 80 (T80; saturating), lactic acid (LAC; crosslinking) and

FIGURE 2

Figure 2.

a), b) and c): Attenuated Total Reflection Infrared Spectroscopy (ATR-IR) of chitosan with a) glycerol (GLY, red), b) sorbitol (SOR, green), and c) lactic acid (LAC, light blue). All of them include spectra of chitosan to additive ratios of 1:0.5 (bright)

KEYWORDS

Chitosan | Waste Valorization | Additives | Biobased Coatings

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