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Thermal properties of fish myofibrillar protein-based films as affected by moisture content

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Myofibrilar protein-based films were developed from a film-forming solution based on fish mince. The thermal properties of these films were characterized by dynamical mechanical thermal analysis and by differential scanning calorimetry as a function of their water content. During a temperature increase, the films produced sudden changes in mechanical property and specific heat, which are classicaly associated with the glass–rubber transition for amorphous materials. The glass transition was about 20°C broad. Increasing the film water content involved a non-linear decrease in glass transition temperature. The thermodynamic theory of the glass transition (i.e. the Couchman–Karasz equation) was inadequate to describe fully the plasticizing effect of water on the films. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Most recent reviews focused on natural polymers have demonstrated the possibility of forming biopackagings from various hydrocolloid-based materials[1–3]. However, applications for these hydrophilic materials are still delayed because of the sensitivity of their mechanical and barrier properties to external conditions (i.e. ambient temperature and relative humidity). The combined effect of temperature and relative humidity on the functional properties is traditionally interpreted in terms of disruptive water–polymer hydrogen bondings in a hydrophilic network[4–6]. Recognition of the role of water as a plasticizer of amorphous biomaterials could be associated with the significance of the glass transition as a physicochemical event[7,8].

The molecular response of a glassy material as the system transforms from a metastable glassy state to an unsteady rubbery state corresponds to a general increase in disorder, free volume and mobility of macromolecules[9]. The glass transition phenomenon is affected by the macromolecular characteristics, such as flexibility, size, length of chains, size and polarity of lateral groups, molecular weight, presence of intermolecular covalent bonds or crystallites and by the presence and contents of plasticizers.

Modifications in molecular organization induce variations of the material physical properties, and more particularly of their thermal, mechanical and dielectrical properties. The glass transition of amorphous materials displays thus a discontinuous change in specific heat against temperature and can then be characterized by differential scanning calorimetry (d.s.c.)[10]. Most studies of glass transitions in food materials have for the most part used d.s.c. but mechanical spectroscopy should yield additional information on molecular motions, intermolecular interactions or cross-link density. Dynamic mechanical thermal analysis (d.m.t.a.) is particularly used in relating structural and viscoelastic properties to the response to temperature, frequency or deformation[8,11–14]. In addition, when the transition is broad or the change in heat capacity is small, d.m.t.a. may allow measurement of the glass transition temperature when it is not possible by d.s.c..

In previous studies[6,15,16], myofibrillar protein-based films were developed and the effect of hydrophilic plasticizer, water content and temperature on their functional properties were studied. The present study was undertaken to investigate the application of d.m.t.a. and d.s.c. in order to characterize the thermal properties of these films at various water contents, and to obtain a better understanding of the glass transition effect for this kind of material.

EXPERIMENTAL

Preparation of fish mince

Washed fish mince was prepared from Atlantic sardines following a method proposed by Cuq *et al.*[15]. Gutted and headed fish were passed through a meat bone separator. The fish mince was washed twice with water, strained in a rotary rinser, passed through a refiner and a screw press, and chopped in a cutter. The fish mince was then vacuum packed in polyethylene bags (500 g) and kept at −23°C for a maximum of one month. The samples were thawed for 24 h at 4°C before experiments.

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