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Influence of equilibrium relative humidity and plasticizer concentration on the water content and glass transition of starch materials

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Sorption behaviour and calorimetric glass transition were measured on cast starch films plasticized with varying concentrations of different components (glycerol, sorbitol, lactic acid sodium, urea, ethylene glycol, diethylene glycol, PEG 200, glycerol diacetate). Precision analysis showed that the water level in samples conditioned at 57% relative humidity reached a minimum for a plasticizer content of 10–20% (dry basis). Starting from 14.8% of water (dry basis) as measured in the amorphous starch–water system, a minimum of 12.7 to 14.4% can be attained according to the type of plasticizer added. Glass transition, as determined on samples conditioned at a constant relative humidity (57%), depended on the type of plasticizer used, although general behaviour was broadly similar for all components except glycerol diacetate. Casting trials performed with this substance revealed an evident phase separation and T_g of starch did not appear really modified by its presence. For glycerol, sorbitol and lactic acid sodium, glass transition was measured with respect to plasticizer and water content. Couchman's relation was applied, which describes the T_g variation of the monophasic polymer–diluant system. The likelihood of phase separation for a high plasticizer level is considered. © 1997 Elsevier Science Ltd.

(Keywords: starch; amylose; sorption)

INTRODUCTION

The elaboration of biodegradable packaging materials containing renewable raw materials is a current research concern. Studies[1–4] have shown that starch is a particularly interesting substrate because it is inexpensive and has a thermoplastic behaviour for the performance of classical technical processes (extrusion, injection-moulding, thermal moulding). The mechanical properties of starch in mean ambient humidity, particularly poor elongation (6%) and a rather high maximal strength (40–50 MPA), are indicative of a vitreous material with a glass transition temperature (T_g) above ambient temperature. It was demonstrated[5] that T_g of amylopectin (branched macromolecule of starch) was lower than T_g of amylose (linear macromolecule) but other studies[6–8] relate the particular interest to use amylose for its beneficial effect on the mechanical behaviour of starch materials. These materials could be used more extensively if the temperature range corresponding to the rubbery plateau were enlarged to include ambient temperature. As with classically produced synthetic polymers, the glass transition temperature of amorphous starch is controlled by adding a plasticizer. Various studies (most of which relate to patents)[9–11] include lists of starch plasticizers which are too exhaustive to allow any understanding of optimization criteria. The purpose of the present work was to investigate the relationship between the glass transition temperature of films produced by the casting method and their residual water content, as well as the nature and concentration of the plasticizer added to the solution. The study of this ternary system is complex because water content at a given relative humidity results from the combined affinities of the macromolecular network and the characteristics of more or less absorbent plasticizers.

EXPERIMENTAL

Materials

Potato starch was generously provided by the Roquette Company (Lestrem, France).

The purities and commercial sources of the different plasticizers used are indicated in the following table.

Plasticizer	Source	Purity
Glycerol	Merck	>98%
Sorbitol	Prolabo	–
Lactic acid sodium	Aldrich	99%
Urea	Panreac	99%
Ethylene glycol	Merck	>99.5%
Diethylene glycol	Fluka	>99%
PEG 200	Sigma	—
Glycerol diacetate + triacetate (1/1)	Fluka	—

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