European Polymer Journal 64 (2015) 229–243

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Surface photo-crosslinking of plasticized thermoplastic starch films

Muhammad Bilal Khan Niazi [a,b], Antonius A. Broekhuis [a,*]

[a] Department of Chemical Engineering, Institute for Technology and Management, University of Groningen, The Netherlands
[b] School of Chemical and Materials Engineering, National University of Science and Technology, Islamabad, Pakistan

ARTICLE INFO

Article history:
Received 7 August 2014
Received in revised form 23 December 2014
Accepted 15 January 2015
Available online 23 January 2015

Keywords:
Retrogradation
Amorphous
UV irradiation
Plasticizer
Spray drying
Thermoplastic starch

ABSTRACT

The study aims to explore ultraviolet (UV) cross-linking as a tool to steer the mechanical properties of malic and citric acid plasticized thermoplastic starch (TPS) based films. TPS films were prepared through compression molding of spray dried amorphous powder. Sodium benzoate (SB) was used as photosensitizer. Under dry conditions (RH0%) all samples maintained their amorphous nature while at RH50% and RH100% retro-gradation was suppressed for all films. The rate of moisture uptake, and as a consequence, the rate of retro-gradation, depends on the concentration of the glycerol in combination with citric and malic acid. UV irradiation had no effect on the degree of crystallinity, improved the mechanical properties and decreased the solubility and degree of swelling. Citric acid plasticized and co-plasticized films showed slightly better mechanical properties before and after UV irradiation treatment compared to malic acid, but citric acid formulations appeared to be very moisture sensitive prior to cross-linking.

1. Introduction

In the recent years, there has been growing interest in the development of bio-based and biodegradable products to reduce the environmental impact of plastic waste. Thermoplastic starch (TPS) is a candidate and is biodegradable, renewable, and low cost. One of the first applications in the plastics market is the use of extruded foamed loose fills, to replace non-degradable petrochemical-based products [1,2]. However, from a product design point of view, there are a number of challenges that seriously limit the development of new applications and need to be addressed before thermoplastic starch based films can actually replace current materials. In particular, the hydrophilic nature and poor mechanical properties of TPS seriously limit new product innovations [2]. Water absorption results in reduction of shelf-life and loss of mechanical properties, which depends on the relative humidity (RH) and initiates retrogradation of TPS products [3].

Numerous studies have been carried out in an attempt to overcome the hydrophilic nature and to improve the mechanical properties and shelf life of thermoplastic starch [1]. In previous study, spray drying of starch/maltodextrin formulations was evaluated as a potential technology for the production of moisture-free amorphous TPS formulations [4]. It was found that variation of the amylose to amylopectin ratio had little effect on the properties of samples dried from solution. Most properties, such as moisture contents, crystallinity, particle size distribution, viscosity and powder flow properties were similar for all solution dried TPS blends. Subsequently, amorphous TPS films were produced containing natural plasticizers, i.e. urea and glycerol, and it was found that low molecular weight plasticizers mix better and inhibited

* Corresponding author at: Department of Chemical Engineering, Institute for Technology and Management, Nijenborgh 4, 9747 AG, University of Groningen, The Netherlands. Tel.: +31 (0)50 363 4918; fax: +31 (0)50 363 4479.
E-mail address: a.a.broekhuis@rug.nl (A.A. Broekhuis).

http://dx.doi.org/10.1016/j.eurpolymj.2015.01.027
0014-3057/

retrogradation. However, reduced retrogradation resulted in loss of mechanical properties: reduced tensile strength and increased strain with moisture absorption [5,6]. The effective mixing followed by drying and film production resulted in film performance different from films produced by classic extrusion technology or solvent casting. The difference in behavior can be explained by more intimate mixing of the ingredients and a reduced role of moisture in the non-spray-dried amorphous systems. Urea as a low molecular weight plasticizer, showed to be a more effective plasticizer than glycerol, i.e. delivered a lower T_g, a lower degree of retrogradation and a higher elongation [6]. Malic acid was identified as a strong anti-retrogradation agent as it inhibited recrystallization of starch over the full range of relative humidity levels i.e. 50% and 100% RH. Malic acid was also found to inhibit the retrogradation of mixed formulations containing the acid and urea, glycerol or maltodextrin. This study again showed that reduced retrogradation leads to high moisture absorption and high strain at break with loss of tensile strengths [7].

On the basis of these studies, the hypothesis was developed that improved TPS based films could be produced if the low retrogradation performance could be combined with low moisture absorption. Radiation processing and chemical derivation has been proposed to produce water-resistant material and preventing degradation. Therefore starches were formulated with carboxylic acids and cross-linking by UV irradiation was considered as a potential technique to improve the performance of the films. In literature, the mechanical properties and dissolution of such cross-linked starch blends showed significant improvement compared to the non-cross-linked films [8–10]. Radiation processing is claimed to introduce covalent cross-linking of polymer molecules and is used to improve the properties of polymer products [11].

Citric acid (CA) and malic acid (MA) are inexpensive and non-toxic chemicals. It has been reported that citric acid [12] and malic acid [7] can form strong hydrogen bond interactions with starch and improve its thermal and water stability, and inhibit retrogradation. However, incorporating both citric and malic acid substantially reduced the tensile stress of the TPS films [7,12].

As a follow-up on previous research with plasticized amorphous starch, a study has been carried out to investigate surface cross-linking of thermoplastic starch films. Sodium benzoate is used as the photosensitizer, as it is known to be photolyzed by UV irradiation. UV light excites and decomposes the photosensitizer to produce radicals upon irradiation and leads to macro-radical combination and cross-linking [3,8].

In this work, we investigated the effect of UV irradiations on the structural and physical properties of amorphous TPS films, obtained via compression molding of solution spray dried powder plasticized by carboxylic acids (malic or citric acid) (Fig 1), and carboxylic acids in combination with glycerol. Special emphasis was placed on retrogradation and mechanical properties of films. In addition to changes in crystallinity over time, molecular interaction and thermal properties of spray dried powder were studied and analyzed by FTIR analysis, differential scanning calorimetry (DSC) and thermal gravimetric analysis, respectively. Water uptake at different humidity levels, retrogradation, and mechanical properties of thermoplastic starch films were also discussed.

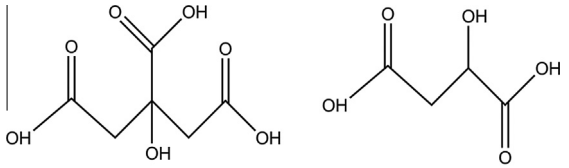

Fig. 1. Plasticizers used for the preparation of TPS powder and films.

2. Experimental

2.1. Materials

Oxidized amylopectin from potato starch (Perfecta-film X-85, moisture content 15% w) was a gift from AVEBE (The Netherlands). Analytical grade glycerol, citric acid and DL-malic acid (99%) were purchased from Sigma–Aldrich. All these materials were used as received without further purification. Codes used for powders and films are depicted in Table 1. The digits in the codes indicate the weight percentage of plasticizer used relative to starch weight.

2.2. Preparation of TPS-powder

TPS powder was prepared as follows. An aqueous solution of starch was prepared by heating 15% (w/w) of dry oxidized starch with different plasticizer contents. Different combinations and ratios (w/w to dry starch) of plasticizer were added in aqueous starch solution and heated to 95 °C for 25 min applying a stirring rate of 600 RPM to prepare homogeneous solutions. The obtained

Table 1
Material codes and corresponding description.

Code	Description (w/w of starch)
U.S	Feedstock material
S.D	Spray dried starch
30G.PS	30% glycerol plasticized starch
30MA.PS	30% malic acid plasticized starch
25G.5MA.PS	25% glycerol, 5% malic acid plasticized starch
20G.10MA.PS	20% glycerol, 10% malic acid plasticized starch
30CA.PS	30% citric acid plasticized starch
25G.5CA.PS	25% glycerol, 5% citric acid plasticized starch
20G.10CA.PS	20% glycerol, 10% citric acid plasticized starch
PS.UV.RH50	Plasticized starch; ultra violet (UV) irradiated at 50% relative humidity
PS.UV.RH100	Plasticized starch; ultra violet (UV) irradiated at 100% relative humidity
PS.UV.SB.RH50	Plasticized starch soaked in sodium benzoate (SB) before ultra violet (UV) irradiated at 50% relative humidity
PS.UV.SB.RH100	Plasticized starch soaked in sodium benzoate (SB) before ultra violet (UV) irradiation treated at 100% relative humidity
SB	Soaked in sodium benzoate
UV	Ultra violet irradiated