Available online at www.sciencedirect.com

SCIENCE DIRECT®

European Polymer Journal 41 (2005) 715–726

EUROPEAN POLYMER JOURNAL

www.elsevier.com/locate/europolj

Biodegradable polymers by reactive blending trans-esterification of thermoplastic starch with poly(vinyl acetate) and poly(vinyl acetate-co-butyl acrylate)

Viktória Vargha [a,*], Patricia Truter [b]

[a] *Department of Plastics and Rubber Technology, Budapest University of Technology and Economics, Müegyetem rkp, 3, H/l, H-1111 Budapest, Hungary*

[b] *CSIR Materials Science and Technology, P.O. Box 395, Pretoria 0001, South Africa*

Received 7 February 2004; accepted 27 October 2004
Available online 13 January 2005

Abstract

Wheat starch was reacted with poly(vinyl acetate) and with poly(vinyl acetate-co-butyl acrylate) in an internal mixer at 150 °C in the absence of catalyst, and in the presence of sodium carbonate, zinc-acetate and titanium(IV) butoxide. The resulted blends were pressed into film and characterized by ^{1}H NMR–^{13}C NMR spectroscopy, differential scanning calorimetry (DSC), mechanical testing, dynamic mechanical thermal analysis (DMTA), thermogravimetric analysis (TGA), and water absorption. Partial trans-esterification took place between wheat starch and the polymers. The blends appeared as homogenous, translucent films with one glass transition temperature range, between that of starch and of the polymer. The presence of wheat starch in the blends improved the mechanical strength of the polymers, although elongation at break severely decreased, which is disadvantageous for processability. Zinc-acetate improved the tensile strength of the blends of starch with PVAC, while all catalysts resulted in an increase in strength of the blends of starch with poly(vinyl acetate-co-butyl acrylate) compared to the strength of the blends without catalyst. Water absorption of wheat starch/copolymer blends was between 150% and 250%, higher than that of the blends with the homopolymer, which was between 100% and 150% after soaking in water. The onset temperature of thermal decomposition was between 290 and 300 °C for all the blends, although the presence of sodium carbonate resulted in a decrease in the onset temperature of thermal decomposition by about 60 °C.

Keywords: Biodegradable polymers; Thermoplastic starch; Reactive blending; Poly(vinyl acetate); Poly(vinyl acetate-co-butyl acrylate); Trans-esterification

---

1. Introduction

Thermoplastic starch would be an ideal matrix for packaging material or one-use articles, because it is a renewable resource material, and biodegradable [1].

---

[*] Corresponding author. Tel.: +36 146 334 76; fax: +36 146 334 74.

E-mail addresses: vargha@muatex.mua.bme.hu (V. Vargha), ptruter@csir.co.za (P. Truter).

doi:10.1016/j.eurpolymj.2004.10.044

Inherent in the chemical structure of starch [2,3], however, the products made from thermoplastic starch are inclined to retrogradation, are sensitive to water, and since water is plasticizer of starch, their performance is unstable, and depends on the moisture content being in equilibrium with the ambient relative humidity. Trommsdorff and Tomka [4] studied the structure of dry amorphous starch on a molecular level by applying an atomistic model, which was in good correlation with experimental results. They extended the model to starch containing different amount of water [5]. Benczedi et al. [6] applied the lattice-fluid hydrogen-bonding (LFHB) model, in order to study the volumetric properties of starch–water mixtures. The experimental data were correlated with the LFHB model, which is able to describe satisfactorily the volumetric behavior of both pure components and of water–starch mixtures. Benczédi et al. [7,8] studied the thermodynamics of amorphous starch–water systems. Their work enables the estimation of the essential properties of amorphous starch, such as glass transition temperature or gas barrier properties.

For extending practical utilization of starch-based products, reinforcement [9] or modification [10,11] of starch is essential. Among the many possibilities of modification, esterification is one of the most important one. Direct esterification [12,13] seems to be the simplest route, although degradation of starch chains is unavoidable resulting in inferior mechanical performance of the end product [14]. Starch–poly(vinyl acetate) materials have been prepared via in situ polymerization of vinyl acetate in the presence of starch by using ferrous ammonium sulfate-hydrogen peroxide redox initiator system [15]. Other methods include melt blending of starch with synthetic polymers, such as poly(ethylene-co-vinyl acetate) and polyethylene with anhydride functionality [16,17].

Goal of this work is to modify thermoplastic starch by reactive blending with polymers containing functional groups, which may react with starch OH groups during the blending procedure via polymeranalog reaction. For this purpose poly(vinyl acetate) and poly(vinyl acetate-co-butyl acrylate) have been selected. The reason for the choice of PVAC was first of all the partial transacetylation of starch with this polymer, in order to reduce its moisture sensitivity. As a result, the formation of a compatible interpenetrating polymer network of starch, of starch acetate and of poly(vinyl alcohol-co-acetate) is expected. The internally plasticized PVAC, i.e. poly(vinyl acetate-co-butyl acrylate), would serve to decrease the glass transition temperature range of the resulting blend. Both polymers are sold as biodegradable by the supplier, and the forming OH groups would enhance their biodegradability. There are three important aspects for attaining positive results via reactive blending. Complete destructurization (gelatinization) of starch, molecular homogenization of the polymeric chains, and adequate energy for the polymeranalog reaction. Therefore gelatinization of starch has been carried out in excess water in the presence of the polymer emulsion in a reaction flask. The homogenous starch–polymer emulsion was dried and the trans-esterification reaction was carried out in the internal mixer in the absence of water at elevated temperature. Experiments have been carried out without using catalyst and in the presence of sodium carbonate, zinc-acetate and titanium(IV) butoxide. Sodium carbonate has been selected for promoting gelatinization of starch, from zinc-acetate and titanium(IV) butoxide catalytic effect to trans-esterification was expected. The blends were tested for chemical structure by ^{1}H NMR and ^{13}C NMR spectroscopy, for mechanical strength, for thermal stability by TGA analysis, for relaxational transitions by DSC and dynamic mechanical spectroscopy, and for swelling in water.

2. Experimental

2.1. Materials

Native wheat starch "A" a product of Szabolcs Starch Ltd. (H-4700 Mátészalka-Vágóháza Hungary) is a white powder of neutral taste, typical odor, with light binding capacity. Amylose content is about 25%. Specifications are the following:

Moisture content:	max. 15% by mass
Ashes:	max. 0.3%
Protein content:	max. 0.5%
SO_2:	max. 0.5%
Acid degree:	max. 20 cm^{3} (0.1 mol NaOH necessary to neutralize 100 g starch)
pH-value:	5–6
Microbiology:	Salmonella/25 g: negative *E. coli*/g: $<10^{4}$ Enterobacteriaceae/g: $<10^{3}$ quantity of microbe/g: $<10^{6}$ mould fungus/g: $<10^{4}$
Storability:	in case of proper storing in dry space unlimited