Polymer Degradation and Stability 101 (2014) 102–108

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

Waterborne polyurethane based starch containing materials: Preparation, properties and study of degradability

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A R T I C L E I N F O

Article history:
Received 6 June 2013
Received in revised form
21 November 2013
Accepted 4 December 2013
Available online 14 December 2013

Keywords:
Anionic polyurethane
Starch
Degradation
Structure
Microorganisms' adhesion

ABSTRACT

New starch-containing aqueous anionic polyurethane dispersions (APU/St) were prepared by the introduction of an aqueous starch solution into an anionic oligourethane solution and by the combination of the chain extension and dispersion stages. A fundamental difference between the APU/St dispersions and mechanical mixtures of anionic polyurethane dispersions and starch (APU + St), which manifests itself in a high aggregate stability and ability to form solid films, has been proved. APU/St based films display higher tensile strength in comparison with St and are characterized by increased values of elongation at break, degree of hydrophilicity, and significantly enhanced ability to undergo an acid/alkaline hydrolysis compared with the APU matrix. The adhesion of microorganisms *Bacillus subtilis* to the APU/St surface, which is the first step and determining factor of biodegradation, exceeds those of the APU matrix. The introduction of St into the APU structure resulted in the formation of amorphous polymer–polymer microdomains, i.e. an integrated system formed due to the presence of both the covalent and the hydrogen bonds between its ingredients. This predetermines the degradation of the APU/St systems as a whole, unlike the mixed APU + St films.

1. Introduction

Economical and ecological problems arising during utilization of polymer wastes by burning and recycling have initiated an advancement of a novel direction in polymer chemistry, namely: creation of pollution-free degradable polymers. The matter concerns polymers and based materials, which degrades into "green" components after completion of the term of their exploitation. One of the ways of research and applied works in this field is to make the existent synthetic macromolecular materials degradable by compounding synthetic polymers with the known renewable degradable components, which serve as a nutrient medium for microorganisms: polysaccharides, in particular, starch (St), and other biodegradable additives. Although these compositional polymers are considered biodegradable, in fact they are not [1,2]. During composting a fast decomposition of the natural component is observed, while the synthetic polymer in most cases is not subjected to degradation. Lately the problem of development of degradable synthetic polymers by incorporation into their composition of natural components is somewhat in a deadlock, which is confirmed by the reduction of the number of publications on subject. More attention is devoted to degradable polymers based on polyesters of hydroxyl carboxylic acids, such as: glycolic, lactic, valeric, caproic [3,4]. For obtaining of corresponding polyesters of pointed acids, their dimeric derivatives – glycoside, lactide in the case of glycolic and lactic acids or β-, γ-, or ε-lactones for the rest of the pointed acids are used.

Considering above-mentioned, this article focuses on the creation of novel ecologically friendly polymers based on polyurethane ionomer and on such available natural compounds as polysaccharides. The ability of polyurethane ionomers (PUI) to spontaneously disperse with the formation of stable water dispersions due to a presence of ionic centers in the macrochain makes them profitably different in comparison with traditional polyurethanes in organic solvents. PUI are commonly used in tanning, textile, paint industry, medicine, agriculture, and other fields of human activity. Their combination with natural polysaccharides (sodium alginate and starch) enables to obtain degradable after completion the term of exploitation polymers, eliminating the formation of toxic products. Both sodium alginate (SA) and starch (St) are natural renewable abundant polymers considered as alternative components in developing degradable materials. Earlier we obtained biodegradable hydrogels based on SA and anionactive polyurethane [5]. The degree of their swelling was controlled by the quantity of added SA and the concentration of introduced Ca^{2+} ions. Such systems are in demand as water-retentive materials with high

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http://dx.doi.org/10.1016/j.polymdegradstab.2013.12.006

mechanical properties. The aim of this work is to synthesize starch modified PUI which in parallel with the inherent to PUI properties will have the new ones, in particular the ability to degradation. Due to the low mechanical properties and high water sensitivity, St is not used as polymer material in its native form. However, due to the low price, degradability and a lot of hydroxyl groups, capable of chemical bonding with urethane prepolymer, St recently is claimed in polyurethane chemistry. The synthesis of degradable polyurethanes PUs is one of developing branch of polyurethane chemistry. Unlike the described in literature technique of preparing polyurethane-starch compositions, namely by mixing their water solutions, or organic solvents, by compression molding, extrusion, using preliminary modified St, (with glycerin, polyoxyethylene glycol) [6,7], we introduced the water solution of pure St to acetone solution of anionic polyurethane prepolymer on the stage of it's elongation and dispersion, thus obtaining the graft copolymer.

2. Experimental

2.1. Materials

Hexamethylene diisocyanate (HDI) (Merck), polyoxytetramethylene glycol (POTMG 1000), dimethylolpropionic acid (DMPA) and triethylamine (TEA) were purchased from Aldrich and used as received; acetone, corn starch (Fluka).

2.2. Preparation of anionic polyurethane

Preparation of anionic polyurethane (APU) (matrix) in the form of aqueous dispersion was achieved by the reaction of POTMG and HDI based isocyanate precursor (component ratio 1:2, reaction time 2 h) with TEA neutralized DMPA, in acetone solution, followed by extension of anionic oligourethane prepolymer with water, dispersion and acetone removal.

2.3. Preparation of starch solution

Corn starch (St) was dried under vacuum at 90 °C for 48 h. Estimated amount of dry St was dissolved with stirring in distilled water at room temperature with following gradual increase of the temperature up to 90 °C. St has been stirred at 90 °C for 20 min (stage of jellification).

2.4. Preparation of starch containing anionic polyurethane

Starch containing anionic polyurethanes (APU/St) were obtained as follows [8]: acetone solution of anionic oligourethane prepolymer (AOU) was dispersed with St water solutions of given concentrations for obtaining finally APU/St with St content of 1.5–35% (wt). Obtained APU/St water dispersions were kept under stirring for 2 h. Whereupon acetone was evaporated with a water-jet pump and obtained St-containing dispersions were stirred for 2 days at 50 °C.

2.5. Preparation of anionic polyurethane-starch mixture – sample of comparison

(APU + St) was prepared by adding of APU dispersion to 15% St water solution under stirring. It should be noted that the film formation was observed only in the case when the mixture was obtained by adding APU dispersion to the St flour paste, however, the film was not heterogeneous, which made it difficult to determine it's basic characteristics. The mixture obtained by adding the St flour paste to APU dispersion did not form the film at all.

2.6. Film formation

APU/St dispersions with different St content and APU + St mixture were poured onto a Teflon substrate. Films were formed during 72 h, afterwards were dried till constant weight in a vacuum oven at 60 °C.

3. Characterization

pH value was determined using pH-meter "pH-150 M" (Russia).

Particle size measurements were determined from the turbidity spectrum using FEK-56M, according to Ref. [9].

3.1. Water absorption

Preliminary weighed dry films of APU matrix, APU/St and APU + St were immersed in water for 1 h and 24 h, whereupon the excess water was removed with filter paper and samples were weighed. Water absorption (W_{H_2O}, wt.%) was calculated according to: $W_{H_2O}(\%) = [(W_w - W_d)/W_d] \cdot 100\%$, where W_w and W_d – weight of the films in a wet and dry state, correspondingly.

3.2. Mechanical properties

Mechanical properties were tested using a RM-30-1 test machine (a device constructed in Ivanovo Measure-works, Russia). The number of samples used in each measurement was three. Samples were prepared in a form of strips (width – 4 mm, operating length – 2 mm). Measurements were carried out in accordance with standard 14236-81; allowed error – 3%.

3.3. Adhesion of microorganisms on the film surfaces

The active strain *Bacillus subtilis* (IMB B–7023), used for microorganisms' adhesion study is highly widespread in nature and possesses a high hydrolytic activity relative to polymer compounds, and may serve as a model of cells-destructors [10]. Adhesion of *B. subtilis* strain to the film surfaces was tested in accordance with [11]. Initial suspension of bacillus cells contains $(1.0 \pm 0.07) \cdot 10^9$ cel/ml. Object plates covered with APU/St were immersed into the liquid nutrient medium by Menkina with preliminary grown microoorganisms' strain and kept for 5 h. Clean object plate and the plate covered with APU without St were used as references. The count up method with the use of polarizing-interference microscope "Biolar" (Polland) was applied. Calculation of microorganisms' quantity was carried out in 50 fields of vision; each contained no less than 15 bacteria cells. Experiments were repeated 3 times for each sample.

3.4. Hydrophilicity

Hydrophilicity of APU/St films was evaluated by measuring the contact angle formed between water drops and the surface of the film. Contact angles were measured with digital camera Olympus C-765 Ultra Zoom and treated with the program Adobe Photoshop 7.0. The drops of water were mounted on 3 different areas of the surface with a microsyringe. Results are the mean value of three measurements on different parts of the samples.

3.5. Degree of hydrolysis in acid and alkali medium

Degree of hydrolysis in acid and alkali medium was determined by weighing the samples before and after hydrolysis. Pre-weighed samples were immersed in 0.1 N solution of KOH and HCl and kept in a thermostat for 30 days at $T = 37$ °C, afterwards the films were dried to constant weight with following control weighing.