A BIODEGRADABLE POLYMER NANOCOMPOSITE:
MECHANICAL AND BARRIER PROPERTIES

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Keywords: plasticized starch, unmodified montmorillonite, biodegradable nanocomposite, mechanical properties, moisture permeability

The preparation of an environmentally friendly nanocomposite based on plasticized potato starch and unmodified montmorillonite clay is described. Data on the influence of montmorillonite concentration on the mechanical properties of the materials obtained are reported. The effective elastic constants of the nanocomposites are calculated. The calculation results are compared with experimental data. The influence of montmorillonite content on the moisture permeability is also investigated.

1. Introduction

The utilization of polymer products upon termination of their service life is a global environmental problem. The traditional ways (burning, recycling, waste disposal, and pyrolysis) cannot improve the ecological situation fundamentally. In this connection, in many countries, intensive elaborations of ecologically safe biodegradable polymer materials for products of short-term application are going on. These materials must degrade quickly enough under the action of the natural environment (soil microorganisms, light, water, and other factors). In developing such materials, mutually contradictory requirements must be met for their rather high parameters of mechanical properties on the one hand and for the accelerated biodegradability on the other hand. The creation of such materials is a topical problem of the modern science of polymer materials.

Considerable attention is being paid to the manufacture of biodegradable synthetic polymers [1, 2]. Materials based on biodegradable natural polymers obtained from constantly renewed vegetable raw material are of ever-increasing interest, too. A special place among them is occupied by starch-based plastics. Starch is a typical natural polymer; it is biodegradable and, after plasticization, can be recycled into articles on the standard processing equipment (extruders, molding machines, etc.) [3]. Glycerin, which is usually used in combination with water, exerts a plasticizing effect on starch. Glycerin is nontoxic, biodegradable, and sufficiently thermostable. The basic drawback of the materials based only on starch and a softener is the rather low indices of their deformation and strength properties and the instability to the action of water. Therefore, recently blend composites containing both natural and synthetic polymers have been widely investigated [3-8]. The starch in such blend materials biodegrades and, at certain ratios of the content of constituents, initiates disintegration (fragmentation) of the composite as

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a whole. The basic difficulties in creating such composites are caused by the poor compatibility of starch with nonpolar and low-polar polymers; therefore, they need an additional refinement to improve the affinity of blend components.

A promising direction in improving the mechanical properties of plasticized starch is the introduction of anisometric (fibrous or lamellar) particles of a filler. In this case, the effect of reinforcement (strengthening) can be reached not only owing to the considerably higher values of strength and rigidity of the fillers, but also to the particle geometry (the characteristic ratio of their sizes, which is also known as the aspect ratio). Positive results were obtained upon using cellulose fibers as the filler. For example, in [9], investigated were composite films made of starch plasticized with glycerin, which contained cellulose microfibrils of diameter ~2-4 nm and length of several micrometers as a filler. The dynamic mechanical analysis (DMA) data obtained in the range of temperatures from –150 to 200°C showed that the introduction of only 5 wt.% cellulose microfibrils made it possible to increase their elastic modulus, at temperatures above the glass-transition temperature, by two decimal orders of magnitude. In this case, the moisture sorption by the material decreased noticeably.

At present, the number of studies dedicated to the investigation of polymer composites containing plane nanoparticles of layered silicates as a filler increases especially rapidly. These materials are called nanocomposites [10]. The silicate used in polymer nanocomposites most widely is the clay mineral montmorillonite. The data in the literature indicate that many parameters of physicomechanical properties of the polymers can be improved noticeably by introducing a rather small amount (usually less than 5 wt.%) of montmorillonite nanoparticles. As the polymer matrix of such composites, many synthetic polymers (polyethylene, polypropylene, polyamides, epoxy resins, elastomers, etc.) have been approved successfully. From the ecological viewpoint, the drawback of the materials is the fact that, after usage, they practically do not degrade under the influence of the natural environment. Therefore, during the last years, an interest in starch-based composites containing montmorillonite as a filler [11-15] has increased. These composites consist of a completely biodegradable matrix and an ecologically safe filler.

In the studies published, different ways of improving the properties of such materials (chemical modification of starch, directed change of technological modes, the choice of optimum structures of compositions, organic modification of montmorillonite, etc.) are investigated. The purpose of the present study is to create a biodegradable polymer composite based on a plasticized starch and an unmodified natural clay and to investigate the relations between the mechanical and barrier properties of the material obtained and the concentration of filler.

2. Initial Materials and Manufacture of a Nanocomposite

In this study, we used a potato starch of density 1.5 g/cm³ and moisture 19.7%, manufactured by Aloja-Starkelsen (Latvia). As a softener, glycerin with a molecular mass of 92.09 g/mol and density of 1.26 g/cm³ was used. The filler was a purified native clay from Vadakste (Latvia) deposits, whose basic rock-forming mineral is montmorillonite (MMT).

The procedure of preparation of the specimens of plasticized starch (PS) consisted in the following. A mixture of preliminary dried starch with glycerin in the mass ratio of 5 : 3 and distilled water was mixed intensively for 30 min at a temperature of 75 ± 5°C. The blend prepared was cast into Petri dishes made of poly(methyl methacrylate) (PMMA) and dried in a heat chamber at 50-60°C. The resulting lamellar preforms were used for preparing specimens.

In manufacturing nanocomposite specimens, the purified clay was preliminary crushed in distilled water, held for 48 h at a temperature of 35 ± 5°C, and dispersed additionally by using ultrasound. Then, the clay fraction prepared was mixed with the corresponding amount of starch, glycerin, and water and blended intensively at 75 ± 5°C for 30 min. The resulting mix was cast in Petri dishes made of PMMA and dried at 50-60°C. Test specimens were cut out from the nanocomposite film preforms obtained. By varying the ratio of the amount of mixed PS and MMT dispersions, we obtained specimens with a different content of filler. In total, four variants of the material with 0, 1, 3, and 6 wt.% MMT were prepared.