



STUDYING THE EFFECT OF INULIN ON THE PROPERTIES OF LOW-DENSITY POLYETHYLENE

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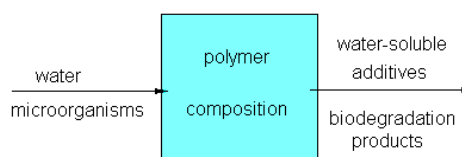
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Abstract

The mixtures of linear low-density polyethylene (LLDPE) with a water-soluble oligosaccharide inulin are obtained, in which the latter is used as a filler that can promote biodegradation. It is shown that the introduction of inulin slightly deteriorates the mechanical properties of the filled polyethylene. The composite material remains stable in water for several days, and during prolonged contact with it, inulin is partially replaced by water containing microorganisms that destroy the composition. The results obtained show that one-stage mixing can afford the material susceptible to biodegradation.

Key words: inulin, water-soluble oligosaccharide, polyethylene, biodegradation, mechanical properties.



Introduction

Polyethylene (PE) is a large-scale industrial polymer. It can withstand the exposure to solar radiation and atmospheric oxygen in combination with the action of heat and moisture in natural conditions for decades without noticeable destruction. This resistance leads to the accumulation of large amounts of polyethylene waste and, undoubtedly, has a negative impact on the environment. However, in some cases it is difficult to find a replacement for polyethylene.

Nowadays, the problem of obtaining biodegradable polymeric materials based on different types of polyethylene, a plastic which occupies the first place in the manufacture of household and industrial products, has acquired particular relevance. The most common way to solve this issue is to introduce a bioorganic filler into the polymer, for example, starch or food industry waste. This leads to a number of positive processes and, first of all, promotes the diffusion of water into the composition. With water from the environment, microorganisms enter the polymer mass that are capable of interacting in an aqueous medium with a bioorganic filler, which serves as a nutritive medium for them. During the whole shelf life of the corresponding products, water washes away the products of biodegradation from the polymer matrix, which leads to the material destruction.

Legon'kova *et al.* [1] showed that different types PE are decomposed by fungal microorganisms under composting conditions. Therewith, the intensity of mycelium development in PE was found to depend on its density: the lower the density of PE, the lower its fungal resistance. This can be associated with easier access of water into PE and, consequently, easier access of soil microorganisms with it.

It is important to note that high-density polyethylene (HDPE) (crystallinity degree of 40%) at 25 °C is characterized by a low diffusion coefficient ($0.36 \cdot 10^{-7} \text{ cm}^2/\text{s}$) [2]. The water absorption capacity of LDPE is 0.02–0.04% for 30 days at 20 °C [3]. Therefore, the decomposition processes of PE products occur mainly in the surface layer and with low rates.

Earlier it was shown that the mycelium of micromycetes randomly aggregates on polymeric materials [4–7]. Fungi are adhesively attached to the surface and form a microenvironment around themselves. The process of biodegradation of polymers is determined by surface damage due to the destruction of both the main chain and side groups, and the additives introduced into the polymer.

Hence, the decomposition of waste PE films as well as the composites based on it takes a long time, which is caused, in particular, by the low diffusion coefficients of water in PE. In the absence of water, biodegradation is practically impossible; therefore, one of the main problems is to develop ways to increase the water absorption capacity of polymer compositions, for example, by introducing bioorganic additives into the polymer.

On the other hand, the introduction of a bioorganic filler leads, as a rule, to a decrease in the strength of the polymer composite and reduces the performance of products made from them during operation. Sherieva [8] reported that the introduction of 1.5 wt % of starch plasticized with glycerol leads to a decrease in the tensile strength (σ_c) by 2 times and relative elongation at break (ϵ_c) by 20 times, whereas at its content of up to 30 wt % the material became embrittled. A similar result was obtained by Thu [9]: the introduction of 30 wt % of rice starch into LDPE led to a decrease in the tensile strength from 15.7 to 8.5 MPa and a decrease in the relative elongation at break from 550 to 11%.

To increase the content of a filler in the composition, thermoplastic starches (TPSs) were prepared: mixtures of native starches with glycerol and sorbitol in 60/30/10 ratio. The TPC rods were obtained by extrusion and introduced into PE. However, the materials produced in this way with a 30% starch content featured the value of ε_c about 100%, which is significantly lower than that for starting polyethylene [10].

This work deals with the production of biodegradable polyethylene composite materials using the biologically active filler inulin (polysaccharide, Fig. S1 in the Electronic supplementary information (ESI)). Its dissolution in water ensures its diffusion into the matrix polymer and creates a nutritive medium for the growth of microorganisms that promote further biodegradation of the composite. The effect of the inulin concentration on the mechanical properties of the PE-based composites, as well as their water resistance and biodegradability in soil were studied.

Results and discussion

Mechanical properties of the PE–inulin composites

In all the composites explored, the inulin particles up to 30 μm in size were uniformly distributed in the polymer matrix. Figure 1 (a) shows a microphotograph of the PE film containing 30 wt % of inulin. The formation of aggregates and clusters of particles is not observed.

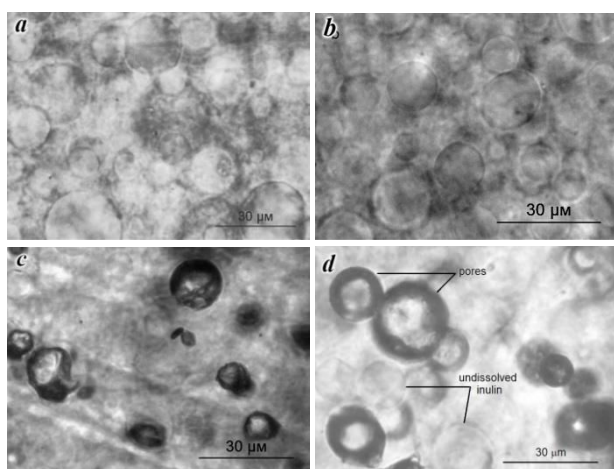


Figure 1. Microphotographs of the films (in transmitted light) with the inulin content of 30 wt %: the initial film sample (a), the sample after exposure in water for 4 (b), 24 (c), and 150 days (d) and subsequent drying under vacuum.

The introduction of inulin into PE does not change its deformation behavior. The composites, as well as initial PE, are deformed with the formation of a neck and decompose at the strain hardening stage. The stress–strain curves of the samples of the compositions explored are depicted in Fig. S2 in the ESI.

Figure 2 shows the dependences of the yield point (σ_y), tensile strength (σ_c), and relative elongation at break (ε_c) of the composites on the inulin content. As the filler concentration increases, the values of σ_y and σ_c decrease linearly, in contrast to ε_c . The values of the latter decrease monotonically in the range from 0 to 30 wt % of the filler, remaining above 800%. Filling PE with 40 wt % of inulin leads to a decrease in ε_c up to 480%.

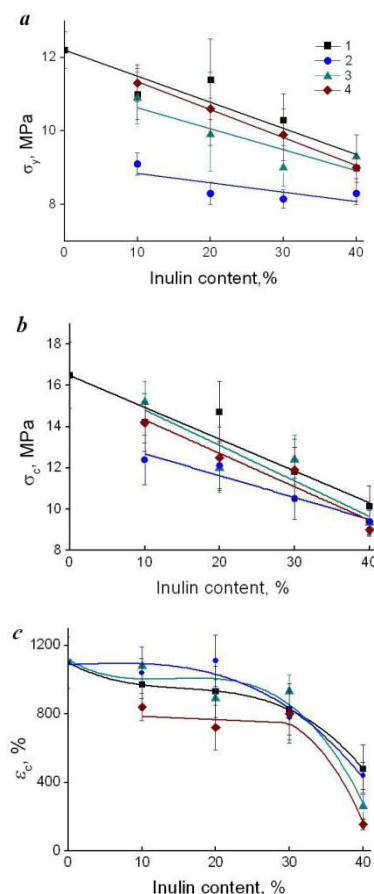


Figure 2. Dependences of the yield point σ_y (a), tensile strength σ_c (b), and relative elongation at break ε_c (c) of the composites on the inulin content: initial mixtures (1, -■-), wet mixtures after exposure in distilled water for 24 days (2, -●-) and then dried (3, -▲-), mixtures after composting in soil (4, -◆-).

The result of maintaining high stress–strain properties of the PE–inulin systems up to 40 wt % of inulin (~31 vol %) may be of great interest, since the introduction of, for example, starch, including plasticized starch, into a polyethylene matrix leads to a drastic decrease in the tensile strength and relative elongation at break of the resulting composites [8–10]. A similar situation is observed when other bioorganic additives are used: beetroot pulp, rice husk, and cocoa shell. The application of inulin as a bioorganic filler for PE allows for avoiding this adverse effect. Moreover, since the relative elongation at break of the compositions with inulin remains at quite a high level (at 40 wt % of inulin, the value of ε_p of the composition is 480%), they are suitable for the production of stretch films.

Water absorption of the PE–inulin compositions

As it was noted above, PE features minimal water absorption. Consequently, changes in the mass of the polyethylene compositions kept in water can be associated with swelling and dissolution of inulin introduced into PE.

Figure 3 (a) shows the kinetic dependences of swelling in water ($\omega_{\text{H}_2\text{O}}$) of the samples containing 10 and 30 wt % of inulin, in the coordinates of the Fick equation. At the first stage (from 0 to 24 days), the dependences of $\omega_{\text{H}_2\text{O}}$ on \sqrt{t} are linear. A further increase in time of the sample exposure in water leads

to a decrease in the water absorption rates.

The swelling of the PE–inulin composites in water is accompanied by leaching of inulin. As an example, Fig. 3 (b) depicts the kinetic dependence of the amount of inulin washed out (ω_{inulin}) from the sample with its initial content of 30 wt %. After 150 days, the content of the bioorganic filler in PE is reduced by 17%.

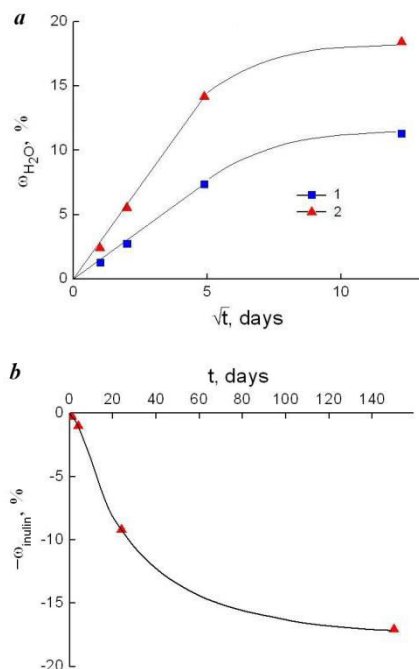


Figure 3. Water absorption of the compositions with different initial contents of inulin (a) and loss (leaching into solution) of inulin (b). The initial inulin content was 10 (–■–1) and 30 (–▲–2) wt %.

Changes in the structure of the films containing 30 wt % of inulin appear in 4 days of exposure in water. Note that prior to microscopic studies, the wet samples were dried to constant weight. An increase in the contour sharpness of a phase boundary (Fig. 1 (b)) indicates the formation of microcavities between the polymer and inulin particles due to the dissolution of the latter and a decrease in their size. After exposure in water for 24 days and more, there are observed voids or pores in the film, along with the particles, which repeat the size and shape of the filler particles (Fig. 1 (c, d)). Obviously, their formation is caused by the dissolution of the inulin particles. It is important to note that, regardless of the content of inulin introduced into PE and the time of exposure of the films in water, a part of inulin remains in the polymer. This circumstance can ensure the biodegradation of the PE composites.

Despite the prolonged exposure of the PE–inulin composites in water and a decrease in the inulin content, their mechanical properties undergo minor changes (Fig. S3 in the ESI). Figure 2 shows the concentration dependences of the upper yield, tensile strength, and elongation at break of the samples kept in water for 24 days and then dried to constant weight. Comparing them with the related dependences for the initial samples, it can be noted that the difference in the values of σ_y does not exceed 1 MPa. The dependence of σ_c on the inulin content in PE coincides with that for the initial compositions. In the case of ε_c , the exception is a film with 40 wt % of inulin. While the initial

samples of this composition decompose at 480% strain at the stage of strain hardening, after exposure in water and subsequent drying, their decomposition occurs at 260% strain during the propagation of a neck to the working part of the deformed sample.

Minor changes in the stress–strain properties of the compared composites suggest that the inulin particles have low adhesion to the matrix polymer and during the deformation of the initial composite after reaching σ_y , a certain content of the filler from the surface layers can be separated from the matrix. Pores should appear in their place. The exposure in water also leads to a slight decrease in the content of inulin (a film with 30 wt % filler loses 10 wt % of inulin within 24 days, which composes 3% of the material mass, Fig. 3 (b)). At the moment of rupture, the material with partially leached inulin is similar to the initial composition, from which a part of the filler separated as a result of stretching.

The mechanical properties of the wet films kept in water and not subjected to further drying were also studied. The dependences of their mechanical characteristics on the initial inulin content are shown in Fig. 2. It should be noted that, in this case, the composites consist of the polyethylene matrix, inulin swollen in water and its aqueous solution. There can also be a residual amount of initial inulin. The presence of water in these compositions leads to their plasticization, which is manifested in a decrease in the yield point and tensile strength (Fig. 2). Taking into account the fact that the work was concerned with the engineering stress values, a decrease in the strength characteristics of the composites may be caused by an increase in the cross-section of the film samples swollen in water. The relative elongation at break of the swollen samples is close to the corresponding values of the initial films.

Thus, inulin as a water-soluble bioorganic filler promotes the diffusion of water into the polymer compositions, and its leaching leads to an increase in the contact surface of polyethylene with the environment. A part of inulin remains in the material and can serve as a nutritive medium for different microorganisms. The mechanical properties of both swollen and dried materials after a long exposure in water change insignificantly.

Properties of the PE–inulin composites after composting

The degradability of the PE–inulin composites in soil was studied. The duration of composting was 24 days. Figure 2 shows the dependences of the mechanical characteristics of the samples after composting on the initial inulin content. There are no significant differences between the upper yield point and tensile strength of the initial samples and the samples after composting. However, the deformation properties of the samples deteriorated after exposure in soil, but remained at the level of 800% at the initial inulin content of no more than 30 wt %.

According to the results of water absorption studies of the samples after composting, during equal time periods, their swelling degree is 2 times lower and their weight loss is 3 times higher than for the composites kept in water, *i.e.*, not exposed in soil.

The microscopic studies revealed branched mycelium and spores of microscopic fungi in the films with a high inulin

content (Fig. 4). The control samples of polyethylene contained only slightly developed mycelium (the microphotographs are not presented). These results confirm the prospects of the suggested approach.

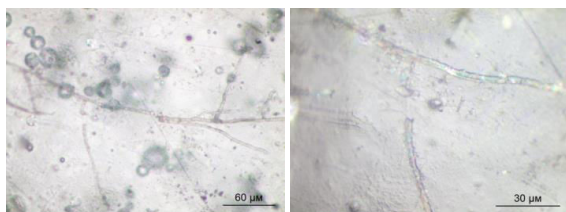


Figure 4. Microphotographs of the films (in reflected light, at different magnifications) with the initial inulin content of 30 wt % after composting for 24 days.

Experimental section

The following materials were used in the work: linear low-density polyethylene (Sabic LLDPE 218 Bj) with a melting point of 114 °C according to the results of thermomechanical analysis (TMA) (Fig. S4 in the ESI); inulin from Beneo Orafiti Senergy 1 (not intended for food and medical purposes), $M_n = 1260$, $MWD = 1.28$ according to the results of GPC studies (solvent DMF + $\text{LiN}(\text{CF}_3\text{SO}_2)_2$). The glass transition and melting temperatures of inulin were 80 and 120 °C, respectively (Fig. S4 in the ESI). The solubility of inulin at 20 °C was 5 g in 100 g of water.

The components were mixed in a Brabender plastograph chamber at 140 °C. The inulin content was 10, 20, 30, and 40 wt %. According to the results of TMA studies, a mixture containing 30 wt % of inulin converts to a viscous-flow state at 117 °C (Fig. S4 in the ESI). Based on this, the temperature of further processing of the mixtures was reduced to 120 °C. The films with a thickness of ~200 µm were obtained by compression molding at 120 °C and 10 MPa, with cooling in a press to 80 °C.

The thermomechanical analysis was carried out on a UIP-70M unit at a constant load of 0.1 MPa. The heating rate was 2.5 deg/min.

The mechanical properties of the films were studied upon uniaxial tension of the samples on a Polyany instrument at room temperature. The working area of the samples was 10 × 2.2 mm. The sample thickness was determined using a micrometer with an accuracy of ±1 µm immediately prior to the experiment. The rate of extension was 0.17 mm/s.

The microscopic studies were performed with a MET-5C microscope (OOO Altami, Russia) in transmitted and reflected light according to the standard method using a plan achromatic lens for bright field PL L 100X/0.85 ∞/0 (working distance 0.40 mm) and Altami Studio software.

The water absorption capacity of the films was measured in distilled water using the following procedure. The films were weighed on an analytical balance with an accuracy of ±0.1 mg, placed at the bottom of a vessel with distilled water (the mass of water was 100 times higher than the mass of the composition), pressed with glass beads to prevent them from floating, and sealed hermetically. The exposure was carried out at room temperature. To determine the amount of absorbed water, the samples were weighed after removal from water. To determine

the amount of washed inulin, the samples were dried under vacuum at 30 °C to constant weight. The mass fraction of absorbed water was calculated using equation (1), and the mass fraction of inulin washed out with water was calculated using equation (2):

$$\omega_{\text{H}_2\text{O}} = \frac{m_2 - m_3}{m_1} \times 100\% \quad (1)$$

$$\omega_{\text{inulin}} = \frac{m_1 - m_3}{m_4} \times 100\% \quad (2)$$

where m_1 is the mass of the initial sample, m_2 is the mass of the swollen sample, m_3 is the mass of the sample after swelling and subsequent drying, and m_4 is the mass of inulin in the initial sample.

Composting of the samples (exposure in soil) was carried out using the containers with moistened soddy-podzolic soil with pH of the water extract of 6.93–6.96 and pH of the salt extract (KCl) of 6.39. The containers with the samples were left outside for 24 days in autumn (air temperature 20 ± 10 °C). Before testing, the samples were removed, cleaned of soil, and additionally washed with distilled water. Then they were placed in a vacuum oven at 30 °C and dried to constant weight.

Conclusions

Taking into account the global trend away from single-use plastic packaging and oxo-degradable plastics, the PE–inulin compositions are of great interest. Long-life plastic products must be thick-walled, and the main task for their biodegradation is to allow water and microorganisms to penetrate deep into the composition. These materials can be recycled, but under unfavorable conditions in the case of composting, their biodegradation will take significantly less time than for initial PE.

A significant drawback of the proposed approach is the high cost of inulin, which is widely used in medicine as a prebiotic. Since inulin has proven to serve as a water-soluble, biologically active filler that only slightly deteriorates the mechanical properties of the composition, it seems reasonable to find an inexpensive replacement for it.

Another approach to address this issue is to produce materials containing small amounts of inulin in the form of a grafted chain or cross-link. This may shorten the biodegradation period of synthetic polymers without compromising their mechanical properties.

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Electronic supplementary information

Electronic supplementary information (ESI) available online: inulin structure; stress–strain and TMA curves of initial PE and its compositions with inulin. For ESI, see DOI: 10.32931/io2319a.

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