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The effect of moisture content and composition on tensile properties of the synthetic polymer/starch composition

Summary — Systems consisted of polyethylene — ethylene/acrylic acid copolymer — starch differing in starch content (20—47 wt. %) were prepared by extrusion. The curves describing time dependence of water absorption have been determined gravimetrically. It has been found that investigated compositions absorbed water in amount proportional to starch content. Tensile properties of the compositions depended on starch content as well as on absorbed water content. Water content (W_t) increase caused decrease in breaking stress (σ_{max}) and linear increase in breaking strain values (ε_{max}). Elasticity modulus (E) values decreased linearly with W_t value increasing, to the boundary value W_m since with E became constant.
Key words: biodegradable plastic, starch, polyethylene, ethylene/acrylic acid copolymer, water absorption, tensile properties.

Packages can be made from different materials, but recent decades a major position has been taken by the materials made from synthetic polymers obtained mainly from the products of processed crude oil. The cost of their production is low, while their functional properties are very good and so is their resistance to environmental influences. Their durability, regarded as a favourable feature, has become a serious ecological and economic problem. The quantity of used packages, which are not degradable in the natural environment, increases steadily. Recycling of synthetic products wastes is not easy because of a wide variety of polymers, which consequently requires a troublesome and labour consuming segregation.

One of the possible solutions of the problem described above is the use of biodegradable products for packages. However, biodegradable products with appropriate functional properties, such as poly(hydroxyalkanoates), polycaprolactons or poly(lactic acid), are much more expensive than synthetic products. It seems a good solution to use both — synthetic polymers and biodegradable natural substances — for this purpose. One of natural products used for package manufacturing is starch, which is commonly found in the natural environment, inexpensive and easy to obtain [1].

The material containing starch gets destroyed when exposed to environmental factors, since due to starch hydrolysis its structure becomes weaker, and after some time, under certain conditions, synthetic polymers contained in the product also undergo decomposition. High starch content in the material makes its properties worse, especially the mechanical ones [2, 3], primarily due to the lack of compatibility between hydrophilic starch and hydrophobic polymer [4], for instance most frequently used cheap polyethylene. Owning to the use of other polymers which improve the compatibility of starch and polyethylene, it is possible to obtain the material of a relatively high content of starch, which can be used for package manufacturing [5]. The results of earlier studies showed that polyethylene content in such material can be limited to 40—50 % without deterioration of functional properties of a whole [6]. However, an unfavourable feature of such material is its ability to absorb large quantities of water from the air high humidity. It also seems quite likely that some mechanical properties of the material depend on the moisture content in the product.

The purpose of this study was to determine the changes in the mechanical strength of biodegradable material made of starch and synthetic polymer related to the dynamics of water absorption from the air of high relative humidity.

EXPERIMENTAL

Materials

— Potato starch obtained from Potato Industry Company at Niechlow.

— Poly(ethylene-*co*-acrylic acid) (EAA), trade name Primacor 5980 (20 % of acrylic acid) delivered by DOW Europe.

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— Low-density polyethylene (PE-LD), trade name Malen E supplied by PKN Orlen.

— Glycerine (pure for analysis) used as a plasticizer.

Sample preparation

Preliminarily prepared composition starch/EAA/glycerine (8:2:2 w/w) were blended in a Brabender extruder with PE-LD in proportions: 3:7, 5:5 and 7:3 [7] and this way plastic films containing 20 %, 33 % or 47 % of starch were made (temperature profile 120/140/160 °C) [8].

Methods

Dumbbells of dimensions 40x20x1 mm were cut from the films and the samples were placed in a Feutron GmbH chamber at 20 °C and 95 % relative humidity. At certain time intervals the moisture content (weight increase) has been determined gravimetrically. The results have been presented as the curves illustrating time dependence of water absorption progress, by samples investigated. Initial moisture content was determined gravimetrically by sample's drying at 130 °C to constant weight.

The tensile strength tests of the material were made by means of Instron 5566 [9], determining the breaking stress σ_{max}, breaking strain ε_{max} as well as elasticity modulus E.

RESULTS AND DISCUSSION

Water absorption

Figure 1 shows the curves of water absorption from the air of relative humidity of 95 % by the samples of three materials containing 47 %, 33 % or 20 % of starch. The process of water absorption is described by the exponential equation (1) [10].

$$W_t = W_0 + \Delta W \cdot \left(1 - e^{\frac{-t}{t_{63}}} \right) \quad (1)$$

where: W_t — *water content after time t*, W_0 — *initial water content*, $\Delta W = W_R - W_0$, W_R — *equilibrium water content*, t_{63} — *time in which 63 % increase* ΔW *occurred.*

The time t_{63} corresponds to full saturation of the material with water after sufficiently long period.

Equation (1) parameters calculated for three samples of different starch (S) content, are as follows:

— for S = 20 %: W_0 = 4.8 %, W_R = 10.9 %, t_{63} = 551 h (correlation coefficient R^2 = 0.99),

— for S = 33 %: W_0 = 7.8 %, W_R = 19.2 %, t_{63} = 54 h (R^2 = 0.99),

— for S = 47 %: W_0 = 11.3 %, W_R = 27.1 %, t_{63} = 8 h (R^2 = 0.99).

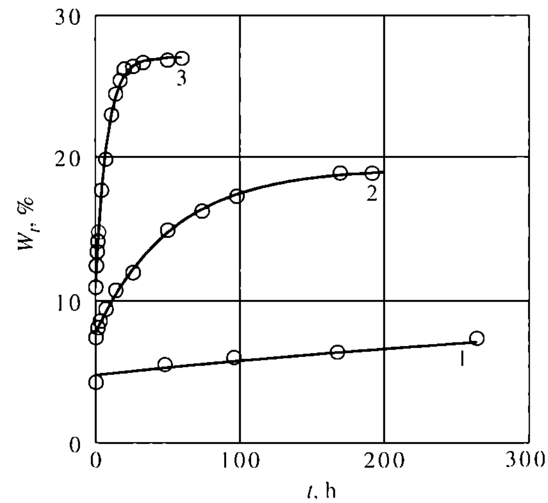

Fig. 1. The effects of time (t) and starch content (S) on water absorption by biodegradable samples: 1 — S = 20 %, 2 — S = 33 %, 3 — S = 47 %; T = 20 °C

As it has been found experimentally, full saturation with water of the material containing 47 % of starch was observed after storing the samples for several dozens of hours in the air of high relative humidity (95 %), whereas a similar level of saturation in the case of the material containing 20 % of starch was observed after almost 2000 hours. This was a result of insufficient access of the water from the air to the deeper layers of starch surrounded by thick membranes of hydrophobic polyethylene. Under such conditions, the diffusion of water to starch, possible in the presence of EAA and glycerine in the system, required longer period of time.

The increase in starch content corresponds with the increased equilibrium water absorption (W_R), from *ca* 11 % of moisture content (S = 20 %) to *ca* 27 % of moisture content (S = 47 %).

W_R values are approximately directly proportional to starch part in the composition.

Tensile strength

The strength of the investigated materials also depends on their composition [11]. The results obtained in the present study show that these properties depend on the moisture content in the material as well. Figure 2 shows the dependence between the breaking stress σ_{max} and water (W_t) as well as starch (S) contents. The increasing W_t values of the material correspond with decreasing breaking stress σ_{max}. In the case of material containing 20 % of starch W_t changes in the narrow range, so this relationship is nearly linear:

$$\sigma_{max} = 8.6 \text{ MPa} - 0.16 \text{ MPa/\%} \cdot W_t \ (R^2 = 0.83) \quad (2)$$

Exponential functions were obtained for the other samples:

$$\sigma_{max} = a + b \cdot e^{-\frac{W_t}{c}} \quad (3)$$

where: a = 2.3 MPa, b = 166 MPa, c = 3.52 % (R^2 = 0.96) for S = 33 %, and a = 3 MPa, b = 26 MPa, c = 4.88 % (R^2 = 0.99) for S = 47 %.

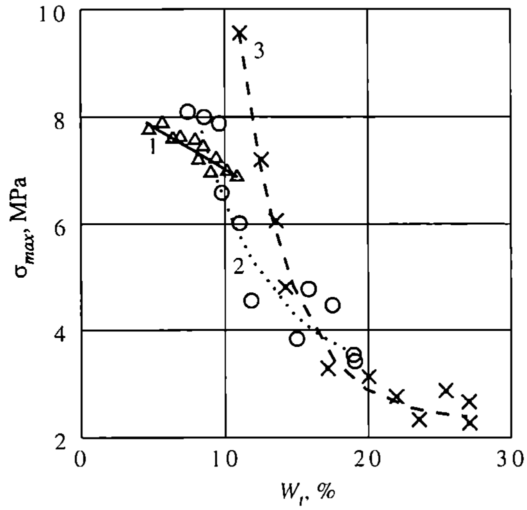

Fig. 2. The relationship between breaking stress (σ_{max}) and water content (W_t) of the materials with different S levels. Descriptions of curves as in Fig. 1

Figure 3 shows the relationship between the breaking strain ε_{max} of the materials of different starch and water contents. The increasing W_t of the material corresponds here in all cases with the linear increase in breaking strain ε_{max}:

$$\varepsilon_{max} = a \cdot W - b \quad (4)$$

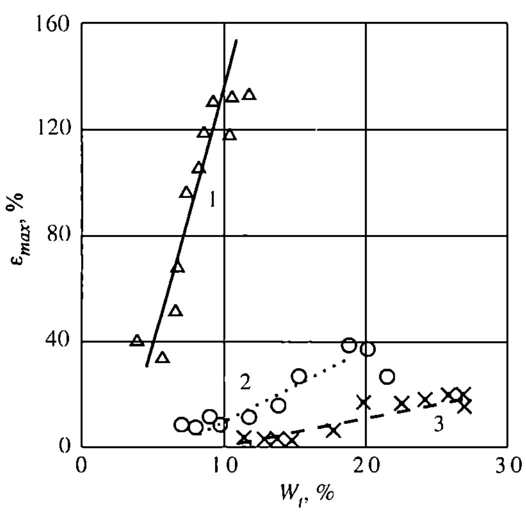

Fig. 3. The relationship between breaking strain (ε_{max}) and water content (W_t) of the materials with different S levels. Descriptions of curves as in Fig. 1

where: a = 19.3, b = 56.5 % (R^2 = 0.87) for S = 20 %; a = 2.7, b = 17.6 % (R^2 = 0.94) for S = 33 %, and a = 1.1, b = 10.4 % (R^2 = 0.92) for S = 47 %.

The highest increase in ε_{max} was observed in the case of material with S = 20 %.

The increasing value of breaking strain and decreasing breaking stress along with the increasing water content were also observed by other authors [5] in their studies on the material containing polyethylene, EAA and wheat starch.

Figure 4 shows the relationship of the elasticity modulus E and moisture content W_t of our materials. Initially E decreases linearly with W_t increasing and then

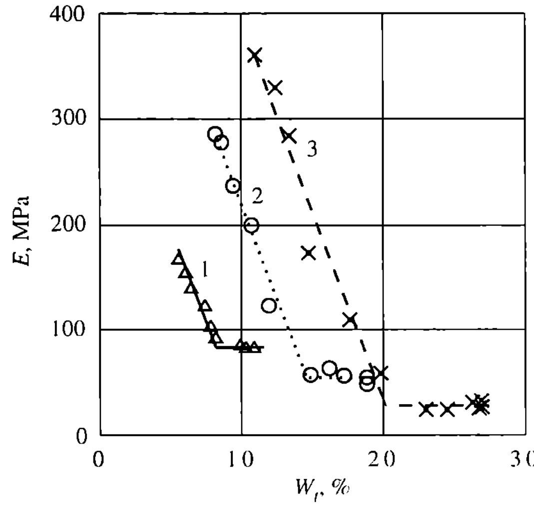

Fig. 4. The effects of moisture content (W) and starch content S in a composition on elasticity modulus (E): 1 — S = 20 %, 2 — S = 33 %, 3 — S = 47 %; E_m — minimum value of elasticity modulus

becames constant. Linear parts of curves are described by the following equation:

$$E = E_k - 36\ \text{MPa/\%} \cdot W_t \ (R^2 \geq 0.93) \quad (5)$$

where: E_k — *value of the elasticity modulus for dry material (W_t = 0).*

E_k increases linearly with starch content in the sample:

$$E_k = 104.7\ \text{MPa} + 13.9 \frac{\text{MPa}}{\%} \cdot S \ (R^2 = 0.99) \quad (6)$$

When the water content exceeded the particular, dependent on S boundary value (W_m), the values of the elasticity modulus were the lowest for this sample (E_m) and no further changes of E were observed (Fig. 4). The W_m values can be calculated using the following formula:

$$W_m = 0.44 \cdot S - 0.67\ \% \ (R^2 = 0.99) \quad (7)$$

The E_m values can be calculated using the following formula:

$$E_m = 122 \text{ MPa} - 2.07 \text{ MPa}/\% \cdot S \ (R^2 = 0.99) \quad (8)$$

CONCLUSION

— Synthetic material containing polyethylene and 20, 33 or 47 % of potato starch absorbed water from the air at the amount approximately proportional to the starch content in the material.

—The time of full saturation of the material with water depended on the amount of starch and ranged from 60 h for starch content 47 % to almost 2000 h for starch content 20 %.

— Tensile strength of the material depended both on the starch and moisture contents.

— The increasing moisture content in the material reduced the breaking stress, while the value of the breaking strain showed a linear increase.

— The values of the elasticity modulus of the material connected with the starch and moisture contents decreased with the increasing moisture content. The increasing starch content in the material, at the range of 20—47 %, resulted in the linear increase in the highest values of the elasticity modulus (E_k) which can be obtained at the moisture content equal 0, as well as linear decrease in the minimum values of the elasticity modulus (E_m) which can be obtained beyond the boundary moisture content (W_m).

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