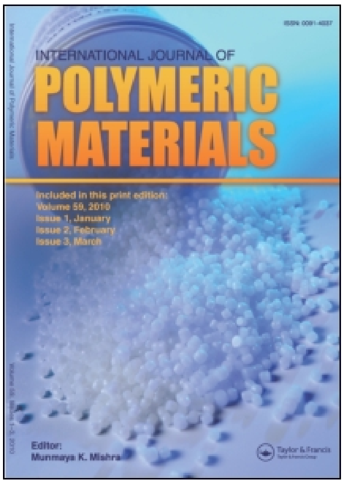

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Effect of Oxidized Polyethylene Additives on Structure and Transport Properties of Polyethylene Porous Films

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Effect of Oxidized Polyethylene Additives on Structure and Transport Properties of Polyethylene Porous Films

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Porous films of high density polyethylene (HDPE) and its blends with oligomeric oxidized polyethylene (OxPE) were prepared. The effect of the additive on porous structure and mechanical properties was investigated. Degree of crystallinity, pore size distribution, specific surface, gas and liquid permeability were measured for permeable samples. Changes in porous structure and mechanical properties of the samples upon changes of additive content have been studied. It was established that oxidized PE additive is located in intercrystalline amorphous regions, and hinders pore formation.

Keywords: extrusion, hard elastic samples, oxidized polyethylene, porous polyethylene film

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INTRODUCTION

It's well known that polyethylene (PE) is very stable to effecting of wide range of oxidants. Its environmental and mechanical properties in addition to good processing by melt extrusion determines its wide spreading. But often it's necessary to modify the surface of PE, i.e. to hydrophilize the surface or prepare it for covering. This can be done only by using of strong agents such as nitric acid, potassium permanganate, plasma [1,2,3].

Usually porous polyethylene films lose their mechanical strength in result of oxidation. It can be explained by that intercrystallite chains most subjected to oxidation. The destruction of sample comes before sensible changes of the surface are observed.

This disadvantage can be overcoming by mixing of polyethylene with some additives in process of film formation. Modification by blending is ancient way to improve the properties of the materials [4], and some interesting effects can be observed at blending of different grades of polyethylene [5,6]. But an additive can change the structure of material and hinder formation of pores. In general any polymer with polyethylene main chain and various end functional groups can be used as additive because it gives a possibility to avoid segregation at processing. In this work the oligomeric oxidized polyethylene with end carboxylic groups was chosen as additive.

The manufacturing process of porous polyethylene films with specific characteristics of surface and porous structure have been elaborated [7]. It was shown that PE porous films prepared in this process are capable to preserve their mechanical properties at covering or formation the polymer phase in the volume of porous sample and on the film surface [8–10]. This process was used to prepare new porous material of linear PE blended with the additive. In this work the effect of the polyethylene oligomer additive on structure, transport and mechanical properties of porous films were investigated.

EXPERIMENTAL

Microporous polyethylene films of HDPE ($M_w = 1.4 \times 10^5$, $M_w/M_n = 6$ to 8 and $T_m = 132^\circ C$) and its blends with additive have been obtained in a process of melt extrusion with subsequent annealing and uniaxial extension. The scheme of the process, which consists of several stages, is presented in Figure 1. The first stage—extrusion—is the film formation when the melt is oriented at a high velocity of flow and then crystallizes at room temperature. At this stage an oriented crystalline structure consisting of a system of large lamellar crystals in the form

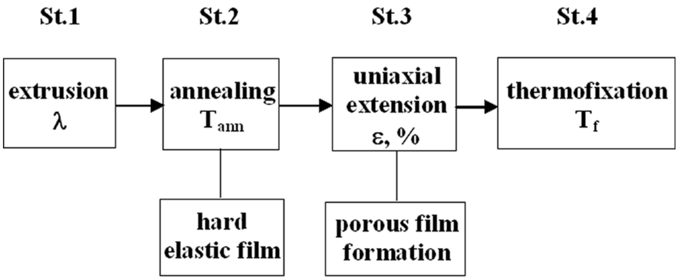


FIGURE 1 Schematic presentation of manufacturing process of PE porous films: λ—spin draw ratio, T_{ann}—annealing temperature, ε—degree of extension, T_f—fixation temperature.

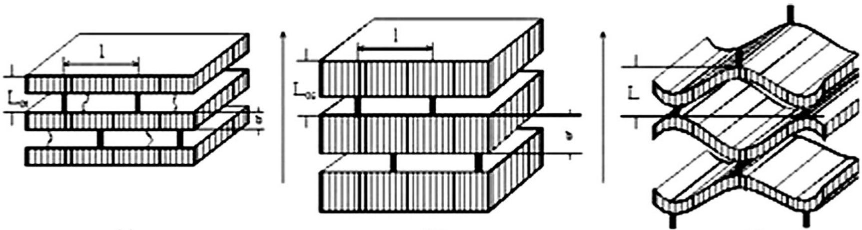
of thin planes arranged parallel to each other and perpendicular to the orientation direction connected with a number of tie chains is formed (Figure 2a).

The orientation degree at extrusion, that is draw ratio λ, was calculated as

$$\lambda = l \times h \times d \times \rho / m$$

where l is length of extruded film (1 meter), *m* is mass of 1 meter of extruded film, and *h, d, and* ρ are thickness, width, and density of extruded film, respectively.

The second stage—annealing at a temperature close to PE melting point under conditions preventing shrinkage of PE—leads to an



(a) (b) (c)

FIGURE 2 Structure model of the samples at the stages of the porous structure formation process: (a) as-spun; (b) annealed (hard elastic); (c) porous structure formation at uniaxial extension (the stretch direction is shown by the arrow). L_{01} is the long period in the initial (as-spun) sample, L_{02} is the long period in the annealed film, L is the long period after extension, b the lamellar thickness, l the distance between ties, d the transverse size of lamellae.

increase in the orientation degree and thickness of lamellae (Figure 2b) due to transfer of molecular chains from amorphous regions into the crystals. As a result, the number of tie chains decreases, they become fully extended, and connect the lamellae as stressed links (hard "bridges") that are statistically distributed over the lamellae surfaces. The mechanical properties of these highly oriented samples can be described as "hard elastic" because they are characterized not only by a rather high elastic modulus, but also by a high elastic recovery typical of elastomers.

These properties make it possible to stretch annealed films several fold without breaking at the third stage of the process. No necking is observed in the stretching. Uniaxial deformation of hard elastic samples in the orientation direction leads to moving apart and bending of lamellae between tie points, and, as a consequence, to the appearance of discontinuities (pores) between them that are caused by specific behavior of crystalline structure under deformation of hard elastic samples (Figure 2c). At increasing orientation degree on the 1st and 3rd stages and also increasing of annealing temperature on the 2nd stage the number and sizes of pores increase [11]. As a result individual pores become interconnected, and flow-through channels appear in the sample. These channels connect two film surfaces and provide permeability for liquids and gases.

The fourth stage is the thermal fixation of porous structure, that is, keeping the sample with fixed sizes for a certain time at elevated temperature for relaxation of stress in the stretched sample. This treatment at the final stage of the porous structure formation precludes shrinkage of the sample after removal of deformation stress. Temperature at this stage of the process controls the thermal stability of porous films, which manifests itself when the porous films show shrinkage from heating [11].

Oxidized polyethylene OxPE (Akdeniz Co., Ltd., Turkey) 12–14 mg/g KOH (MM 9,300–10,000) was used as an additive.

Porous films were obtained using HDPE with content of additive up to 10% in the formation process; the granules of materials were blended in the container of extruder at room temperature, then the blend was melted in extruder and film was formed from the melt.

X-ray measurements were carried out by DRON −2.0 (Saint-Petersburg, Russia) at CuKα-irradiation. Degree of crystallinity was determined by wide-angle X-ray scattering (WAXS).

Microfiltration cell technique was used to determine pore size distribution and to measure permeability of porous films by flowing of N_2, ethanol, and water.

Overall porosity was measured gravimetrically.

Specific surface of porous films was determined by sorption/desorption of N_2 (Sorbtometr-M, Novosibirsk, Russia).

Mechanical characteristics of samples were measured with a tensile test machine P-5 (Ivanovo, Russia).

Contact angle was measured by lying drop technique.

RESULTS AND DISCUSSION

Porous films were formed of HDPE and its blends with OxPE at various additive concentrations and extrusion draw ratios λ. Blends with content of 1, 3, 6, and 10% OxPE were prepared.

It was observed that polyethylene with additive concentration of 10% cannot be extruded. When oxidized polyethylene concentration was 6% the films obtained at annealing completely lost mechanical elasticity and capability to deform—porous films could not be prepared. At contents of additive of 3 and 6% the porous structure was formed but the films did not contain a through-flow pores, and they were impermeable for liquids. At last, at content of 1% OxPE permeable porous films were obtained.

Overall porosity was measured for the films obtained of HDPE and blends with OxPE content of 1 and 3% of additive. It is seen at Figure 3 that overall porosity increases with λ for all samples. The values weakly differ for both blends but they are considerably lower at admixture of oxidized PE than the samples of HDPE without additive.

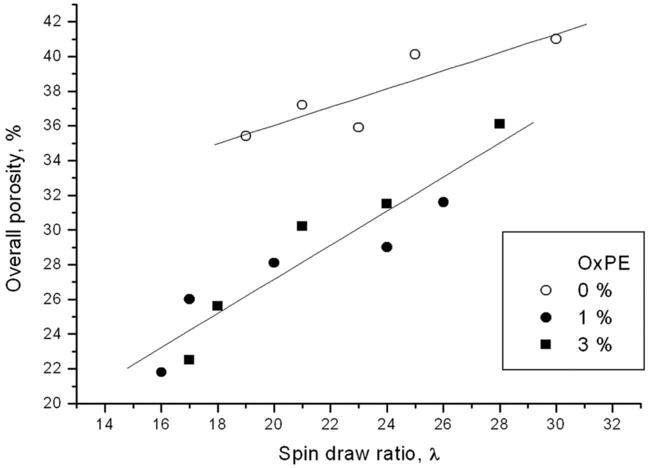


FIGURE 3 Dependence of overall porosity on spin draw ratio λ for porous samples with various content of OxPE (%).

In order to clear up what is the influence of additive on the characteristics of porous structure, the through pore size distributions [12] were measured. The distributions for the films of HDPE and 1%-OxPE blend extruded at spin draw ratio $\lambda = 25$ are presented at Figure 4. Maximum on the distribution for HDPE corresponds to 180 nm, and the major part of through pores ranges in sizes from 140 to 450 nm. Porous films obtained from 1%-blend with OxPE show the same type of distribution but the maximum is displaced to 120 nm and the major part of through pores ranges in size from 80 to 300 nm. It means that admixture of OxPE, even at very low concentration, leads to decreased through pore sizes. It is possible to conclude that the functional groups are concentrated in the amorphous regions as a result of crystalline structure transformations at extrusion and annealing stages. The additives may be placed on the walls of pores lowering their size.

The dependences of gas permeability and liquids fluxes (ethanol and water) on spin draw ratio λ were measured for porous samples. It is seen in Figures 5 and 6 that these values increase with λ for all samples. However, Figure 6 shows that filtration properties of porous films gradually decrease with concentration of OxPE. When it is run up to 3% the films have a rather low permeability even at high values of λ, in spite of considerable overall porosity as shown in Figure 3.

At low contents of additive (1 and 3%) the films are permeable but their permeability is lower than one for the films of HDPE alone. Increasing the additive content leads to a sharp decrease of permeability (gas and liquids) and overall porosity (Figures 3, 5, and 6).

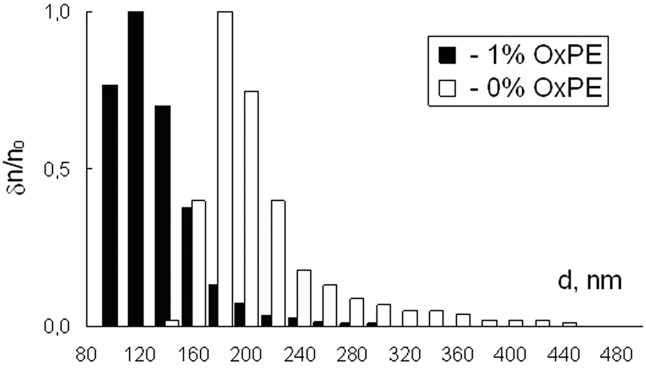


FIGURE 4 Through pore size distribution for porous samples of HDPE and 1%-OxPE blend, d—diameter of pores, $\delta n/n_o$—portion of pores with variable diameter related to the number of pores with the most probable size (n_o).

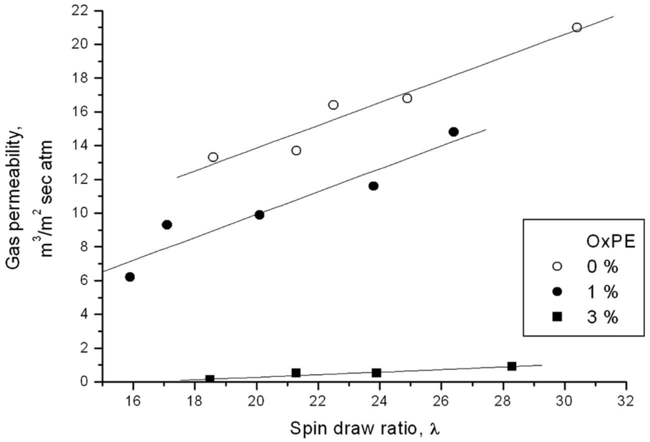


FIGURE 5 Dependence of gas permeability (N_2) on spin draw ratio λ for porous samples with various content of OxPE (%).

This fact correlates with the data of Figure 4, which demonstrates diminished through pore sizes.

It was established recently [8] that porous films formed by this process have a strongly developed relief-like surface. As a result they are characterized by very high values of specific surface. This value was measured for porous films of HDPE and for the samples with

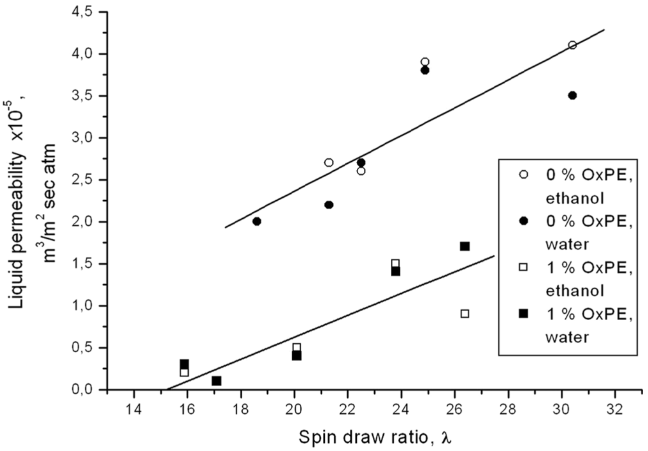


FIGURE 6 Dependence of permeability for liquids (ethyl alcohol and water) on spin draw ratio λ for porous samples of HDPE and 1%-OxPE blend.

content additives 1%. Figure 7 shows that it increases with spin draw ratio λ for both types of samples but it is lower for the films of HDPE/OxPE than for ones of HDPE alone. Decreased specific surface for less permeable samples is explained in that (as it was shown in reference [13]) surface relief becomes more developed and consequently specific surface increases, when the number and sizes of through channels (and through permeability) increase.

It was proved in earlier investigations [11,14] that porous structure formation during stretching of the annealed samples (Figure 1) is determined by hard elastic properties of these samples. Mechanical behavior of hard elastic systems can be demonstrated by the stress-strain curve (Figure 8). There are two modes of deformation while stretching hard elastics (Figure 2): (1) reversible deformation of lamellae network and viscoelastic deformation of tie chains connecting lamellae, and (2) irreversible deformation determined by changes of the lamellar network as a whole. Once the extension is stopped (point C, Figure 8), the stress almost immediately drops to the stress corresponding to elasticity of the lamellar network (point D in Figure 8). During the recovery process the stored elastic energy of lamellar bending is released, and the stress goes down. For an ideal lamellar network, this process should be described by a linear dependence passing through the points D and M, where the position of point M characterizes the fraction of elastic recovery in the total value of deformation. However, the macromolecular chains with extended

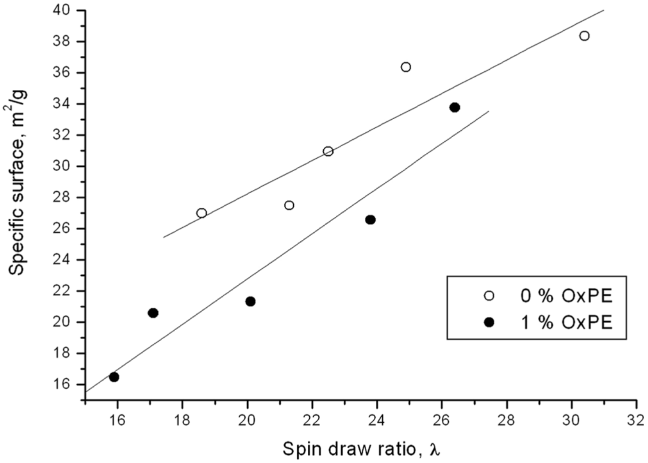


FIGURE 7 Dependence of specific surface on spin draw ratio for porous samples of HDPE and 1%–OxPE blend.

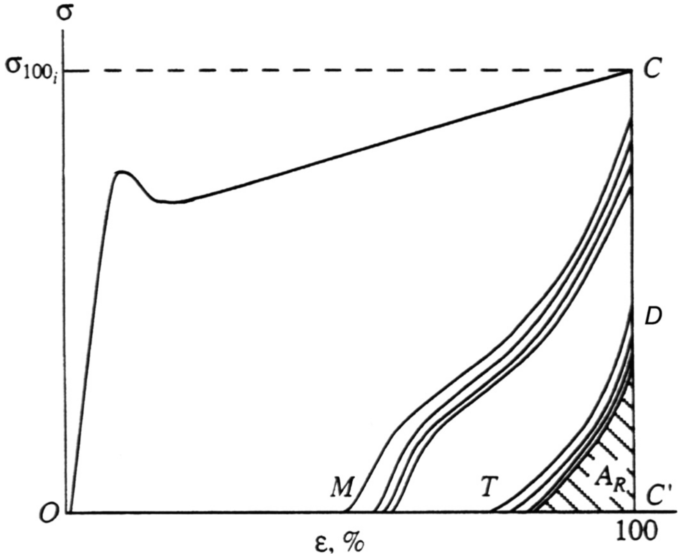


FIGURE 8 Stress-strain curves at cyclic extension for hard elastic samples: σ_{100i}—stress at maximal extension in the first cycle, E_R—elastic recovery (ratio MC′/OC′), A_R—work recovery (dashed part of the curve CC′T), A_R/A_D the portion of work recovery in the full work at extension (ratio of areas CC′T/MCC′ in the cycles following the first one and the ratio CC′T/OCC′ in the first cycle).

conformations (as a result of extension), between the regions of lamellae that have moved apart, hinder fast recovery of the initial form of lamellae because any conformational change is a relaxation process and requires a certain time. The process of strain recovery is characterized by a certain rate, and stress-strain curve is therefore located below the straight line DM and intersects the abscissa axis in point T. The value of elastic recovery E_R is determined by MC′ fragment and equal to the ratio of MC′ to total tensile strain OC′: $E_R = MC'/OC'$ The value of E_R appears to be rather high for hard elastics and reaches 40–60% whereas usually this value for flexible-chain polymers is only 5–10%.

Elastic recovery E_R and work recovery A_R (Figure 8) are very important characteristics of annealed samples because they are responsible for the number and sizes of through pores appearing upon stretching of hard elastic films at the pore formation stage of the process (Figure 1). The authors have analyzed the stress-strain curves of cyclic deformation of annealed samples prepared of HDPE and

HDPE/OxPE. It is measured that E_R for HDPE samples is 40% but it drops to 30% for blends. Work recovery at deformation of annealed films of HDPE and 1%-OxPE blends was 30 and 29%, respectively. But it decreases to 20% for 6%-OxPE blends. Note that only the samples with additive content less than 3% contained through pores.

To analyze the changes in crystalline structure of samples at each stage of porous film formation process (Figure 1) X-ray investigations of the extruded, annealed, and porous films of HDPE and its blends with OxPE were carried out. It was found that the thickness of crystallites did not depend on spin draw ratio and additive content and it was equal to 156 Å.

The dependences of degree of crystallinity (WAXS) on additive content for extruded, annealed, and porous films (Figure 9) have a character typical to the systems formed in the process presented at Figure 1: degree of crystallinity increases after annealing for all samples, and it decreases after extension of annealed samples at the pore formation stage, because of increasing distance between lamellae in the process of extension. But the most interesting fact is that the crystallinity of extruded, annealed, and porous samples of blends is higher than one for the samples of HDPE alone. This result may be related to segregation on molecular masses at crystallization [15] when polymers with different MM crystallize separately because the low molecular fraction is forced out of polymer crystals. It is possible to suppose that the additive located in pores and intercrystalline regions between lamellae of HDPE is capable to form additional crystalline phase that increases

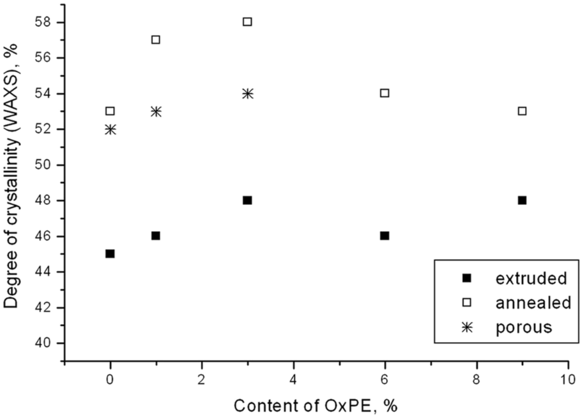


FIGURE 9 Dependence of degree of crystallinity (WAXS) on OxPE content for extruded, annealed, and porous samples.

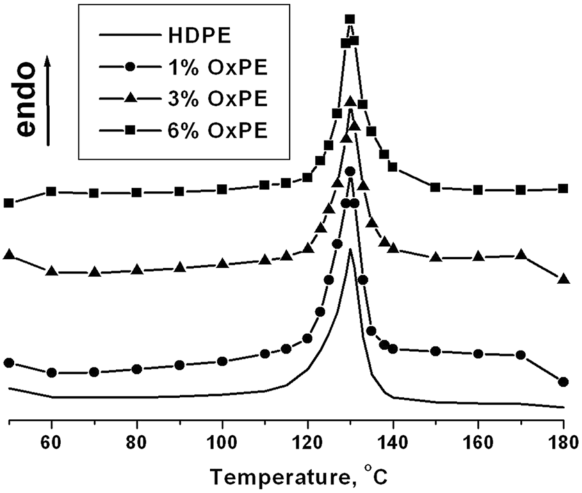


FIGURE 10 DSC curves for annealed samples of HDPE and blends HDPE/OxPE.

the total degree of crystallinity. Some decrease of crystallinity for annealed samples at high contents of additive may be related to the competition between formation processes of crystalline phases HDPE and OxPE, which becomes more pronounced at increased additive content.

Similar results were obtained by DSC measurements of crystallinity, which demonstrate the same path of dependences on λ as WAXS data but the growth of degree of crystallinity for annealed samples is more significant. DSC curves for HDPE and blends HDPE/OxPE are presented in Figure 10. It is seen that the additive does not affect the melting point of the samples because additive content is very low. However, degree of crystallinity (α) and heat of melting ΔH_m for annealed samples increase at growth of OxPE content (Table 1). It

TABLE 1 DSC Data for Samples of Annealed Films of HDPE and Blends With OxpE

% OxPE	T_m, °C	T_{cr}, °C	ΔH_m, J/g	λ, %
0	130	106	162	55
1	130	106	177	60
3	130	105	182	62
6	131	106	190	65

TABLE 2 Mechanical Characteristics of HDPE and HDPE/OxPE Porous Films

	Orientation direction			Transversal direction		
Content of OxPE, %	σ, MPa	ε, %	E, MPa	σ, MPa	ε, %	E, MPa
0	90	135	300	13	9	600
1	130	115	400	16	8	800

may be explained by the contributions of oligomer crystalline phase to these values.

The effect of additive on mechanical properties of porous films was investigated. It was observed that these properties do not depend on spin draw ratio. It is seen in Table 2 that the breaking strength and elastic modulus of porous films formed of 1%-OxPE blends is higher and break elongation is lower than these values for the samples of HDPE alone in both the orientation and transverse directions. This result correlates with the data that porous films of blends have a higher degree of crystallinity than films of neat HDPE.

Contact angle was 94° for all porous samples and it did not depend on OxPE content in the range of OxPE concentrations used in this work. This fact may be explained in that the concentration of additive is very low and most of it is concentrated in pores and intercrystalline regions but not on the sample surface.

Properties of HDPE and its 1%-blends with OxPE porous films are summarized in Table 3.

TABLE 3 Characteristics of HDPE and HDPE/OxPE Porous Films

	HDPE	**HDPE/1% OxPE**
Thickness, microns	10÷15	10÷15
Overall porosity, %	40	35
Breaking strength, MPa	90	130
Break elongation, %	135	115
Specific permeability, measured by filtration porosimetry (ethanol flux), $m^3/m^2\cdot sec\cdot atm$ or $(l/m^2\cdot hour\cdot atm)$	$4\cdot 10^{-5}$ (200)	$1.8\cdot 10^{-5}$ (85)
Permeability, measured by nitrogen flux, $m^3/m^2\cdot sec\cdot atm$	21	15
Maximal size of through pores, microns	0.45	0.30
Size of through pores corresponding to maximum of size distribution, microns	0.16÷0.20	0.10÷0.14
Specific surface, m^2/g	38	32

CONCLUSION

In this investigation the possibility to prepare permeable porous films of HDPE with oxidized PE additive was demonstrated. It was discovered that films with additive concentration more than 10% cannot be extruded, and samples with content of additive more than 3% are impermeable to liquids. It is proved by structure investigations that oligomeric oxidized PE additive is located in intercrystalline amorphous regions in the annealed samples, and hinders pore formation at the stretching stage. Higher degrees of crystallinity of the samples HDPE/OxPE in comparison with neat HDPE films indicate that a crystalline phase of OxPE inside the pores is formed. The appearance of this phase is the result of segregation processes during crystallization of blends containing high molecular PE and its functionalized oligomer. The formation of additional crystalline phase inside the pores leads to diminished pore sizes and decreased permeability of gas and liquids.

It is known that blends usually have poorer mechanical properties than homogeneous systems. However, it is apparent that mechanical properties of the authors' porous samples of blends are higher than ones for films of neat HDPE. This result is related to the increased degree of crystallinity in the samples HDPE/OxPE.

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