
MECHANICAL PROPERTIES, PHYSICS
OF STRENGTH, AND PLASTICITY

Changes in the Structure and Mechanical Properties of Hard Elastic and Porous Polypropylene Films upon Annealing and Orientation

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Abstract—The effect of the annealing temperature on the characteristics of hard elastic polypropylene samples obtained by annealing of extruded films and having an oriented lamellar structure is studied. It is established using the methods of X-ray scattering and differential scanning calorimetry that the lamellae thickness, the large period, and the degree of orientation of the folded lamellae increase with an increase in the annealing temperature, which is accompanied by an increase in the melting temperature and enthalpy. Porous films are obtained by uniaxial extension of the annealed samples in the orientation direction. It is shown that the porosity and permeability of the porous films increase with an increase in the annealing temperature, owing to an increase in the number and sizes of the through channels. The mechanical characteristics (strength, elastic modulus, and break elongation) of the hard elastic and porous films are measured, and their relationship with changes in the structure and orientation of the samples, depending on the annealing temperature, is established.

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1. INTRODUCTION

The ability to form supramolecular structures with a large variety of structural elements, such as crystallite types, their spatial arrangement, size and degree of connectivity, orientation and degree of defectiveness, is a characteristic feature of the polymer systems obtained from crystallizable flexible-chain polymers, in particular polyolefins (polyethylene and polypropylene). The key characteristics of the supramolecular structure of samples depend on the method of its formation, namely, the conditions of crystallization and subsequent processing, such as the orientation drawing and thermal annealing [1–4]. The structural organization determines the physicochemical properties of polymeric materials and, accordingly, the field of their application. Hence, the study of the influence of the preparation process parameters on the structure and characteristics of samples is of interest from both the fundamental and practical points of view.

The possibility of varying the supramolecular structure of flexible-chain polymers in a wide range makes it possible to obtain materials with various combinations of properties and characteristics. Thus, it is known [3, 5] that the defects in the polymer amorphous-crystalline structure lead to a decrease in the strength characteristics of samples. At the same time, porous films preparation methods of such polymers

have been developed [6–10], including the controlled initiation of defects (pores) to obtain the necessary number and sizes depending on the chosen purpose, while maintaining a sufficient level of mechanical strength and elasticity. The process based on extrusion of the polymer melt is the most promising method for the preparation of porous polyolefin films, because it is environmentally safe (as opposed to solvent methods where toxic solvents are used) and technologically efficient. In this process, the initial structure of the sample is formed by crystallization of the extruded film in air after exiting the die. The extruded samples consisting of lamellar crystallites and having an oriented structure owing to the spin drawing are subjected to annealing under isometric conditions (with fixed ends of the sample) to prevent their shrinkage upon heating. The purpose of annealing is to improve the crystal structure due to involving of chains from the amorphous part into the crystallites and, as a result, an increase in the number of stressed tie chains that are capable to keep a load [10–14]. Such samples exhibit the so-called “hard elastic” properties, i.e., the capacity for large elastic recovery and also high elastic moduli. The porous structure in this process is formed during the subsequent uniaxial extension of the hard elastic films, which leads to moving apart of the crystallites and the appearance of discontinuities between

them, i.e., pores (because of emptying of the amorphous part). The possibility of obtaining porous samples and, in particular, permeable films, i.e., the films containing through channels, and their characteristics depend on the structure of hard elastic samples, namely, on the crystallite sizes and also their degree of orientation.

The aim of this work is to study the effect of the annealing temperature, which is the basic controlling parameter at the annealing stage, on the crystal structure of hard elastic and porous polypropylene (PP) films and their mechanical properties.

2. EXPERIMENTAL

2.1. Objects and Methods of Study

Grades of isotactic polypropylene PPG 1035 (Stavrolen, Russia) with a molecular weight of $M_w = 380000$ and a polydispersity of $M_w/M_n = 4-5$ were used to prepare the films.

The films were formed using a SCAMIA laboratory extruder (France) equipped with a slit die with a gap of 1.5 mm at a temperature of 200°C for the melt at the exit from the extrusion head. The polymer was crystallized in the air. Films extruded at spin draw ratio $\lambda = 78$ (the ratio of the film taking rate to the speed of its exit from the extrusion head) were used in the study.

The extruded films were subjected to isometric annealing (under the conditions of fixing film ends) for 1 h with varying the annealing temperature (T_{ann}) from 149 to 170°C.

Porous films were obtained by uniaxial extension of the annealed samples, which was carried out at a rate of 200%/min to a deformation degree of 200% at room temperature.

To prevent shrinkage of the films after removal of the tensile stress, they were thermally stabilized by exposing in isometric conditions for 1 h at a temperature of 130°C.

A study of the hard elastic samples by the method of wide-angle X-ray scattering was carried out on a modified installation DRON 2.0 diffractometer (Burevestnik, Leningrad) using a CuK_α radiation. The recording was performed in the transmission mode. The small-angle X-ray scattering measurements were carried out using a KRATKI camera with an entrance slit of 60 μm ; the primary beam divergence was 3.5 min. The degree of crystallinity, the large period, and the angle of disorientation of crystallites were determined.

The degree of orientation of the samples was characterized by the orientation factor f_c , which was calculated from the following equation:

$$f_c = [3(\cos^2 \varphi)_m - 1]/2,$$

where φ the angle between the orientation direction and the direction of molecular chains in crystallites.

For highly oriented systems, the $(\cos^2 \varphi)_m$ value coincides with the $\cos^2(\varphi_m)$ value; φ_m is determined by the half-width of the azimuthal intensity distribution curve.

The influence of the annealing temperature on the characteristics of the crystal structure (melting point, degree of crystallinity, and enthalpy of melting) for hard elastic and porous films was investigated by differential scanning calorimetry (DSC). The measurements were performed on a DSC 204 F1 calorimeter (NETZSCH, Germany) in an inert medium (argon) at a heating rate of 10°C/min. The heat of melting an ideal PP crystal (165 J/g) was used to calculate the degree of crystallinity [15].

Mechanical characteristics of the samples were calculated from stress-strain curves obtained on a 2166 R-5 tensile machine (Tochpribor, Ivanovo, Russia). The strength, elastic modulus, and relative deformation at break were measured under uniaxial extension of the samples at a rate of 100%/min.

The values of the elastic recovery ER_{100} for hard elastic films were determined under cyclic loading up to deformation ratio of 100% at a rate of 100%/min.

The sound propagation velocity was measured using a PPM-5R Pulse Propagation Meter (H.M. Morgan Comp., United States). According to the measurements of propagation velocity of longitudinal sound waves (10 kHz), transmitting through the film, the polar diagrams of the sound pulse propagation velocity were obtained. At the recording of diagrams the direction 0–180° was chosen along the direction of film extrusion.

The porous films were characterized by the overall porosity, permeability, and pore size values. The overall porosity (P) of the samples (the fraction of the sample volume occupied by the pores) was calculated from the ratio of the density of the studied samples and the known density of a nonporous polypropylene film, as follows:

$$P = [(\rho - \rho_n)/\rho] \times 100\%,$$

where ρ is the density of a nonporous polypropylene film (0.9 g/cm³), and ρ_n is the density of a porous film, which were calculated as the ratio of the film weight to its volume for the sample with dimensions of 50 × 90 mm. The film thickness was measured with a Vogel 0-50 × 0.001 digital micrometer (Germany). The sample mass was determined by weighing.

The permeability (G) of the films to liquids was determined from the flow rate of the liquid wetting PP (ethanol) under a pressure of 0.5 MPa through a porous sample put in a filtration cell and calculated by the following formula:

$$G = V/(S\tau pK),$$

where V is the volume of a liquid flowing through a porous film with an area of S in a time period of τ

under a pressure of p , and K is the filtration cell constant.

The size distributions of through channels were obtained by the method of filtration porosimetry measuring the flow of a nonwetting liquid (the 30% ethanol–water mixture) through the film as a function of the pressure [6, 16].

3. RESULTS AND DISCUSSION

3.1. Formation of the Structure of Hard Elastic PP Films as a Result of Annealing

In the process used to prepare porous films, including extrusion, annealing, uniaxial extension, and thermal fixation [8, 17], the supramolecular structure of hard elastic samples formed at the annealing stage determines the result of pore formation upon their subsequent uniaxial extension. When the extruded films are annealed, their structure consisting of folded lamellae disposed parallel to each other and perpendicular to the direction of the melt flow (orientation direction) is transformed. Folded crystals are a metastable crystallization form, while the equilibrium form is represented by crystals with fully extended chains. However, when crystallization takes place under the conditions of high supercooling (at room temperature), the equilibrium form is not available, because of kinetic reasons for flexible-chain polymers, whose molecules have the coiled form in the melt, so they crystallize in a kinetically more accessible folded form. Upon annealing at high temperatures, at which the motion of chains in crystallites begins, it becomes possible to rearrange them towards the equilibrium state. Lamellae parallel to each other form stacks interconnected by ties of various degrees of tension.

A study of the structure of hard elastic samples as a function of the annealing temperature was carried out by the method of X-ray scattering. As is seen from Fig. 1, the transformation of the structure with an increase in the T_{ann} is becoming ever more effective owing to an increase in the mobility of chains in crystallites, which leads to an increase in the thickness of the lamellae and in the large X-ray period (the sum of the lamella thickness and the size of the amorphous region in the orientation direction). Studies have shown that the thickness of the lamellae does not depend on the annealing temperature until reaching a temperature of $T_{\text{ann}} = 130^\circ\text{C}$, which agrees with the data of dynamic mechanical analysis showing that the motion of chains in polypropylene crystallites becomes possible at temperatures of $130\text{--}140^\circ\text{C}$ [17], so the changes in the structure are observed at $T_{\text{ann}} > 140^\circ\text{C}$ (Fig. 1). According to the X-ray scattering data, the annealed samples have a higher degree of crystallinity than the extruded ones (51%), and this value increases from 56 to 62% in the range of T_{ann} from 150 to 170°C .

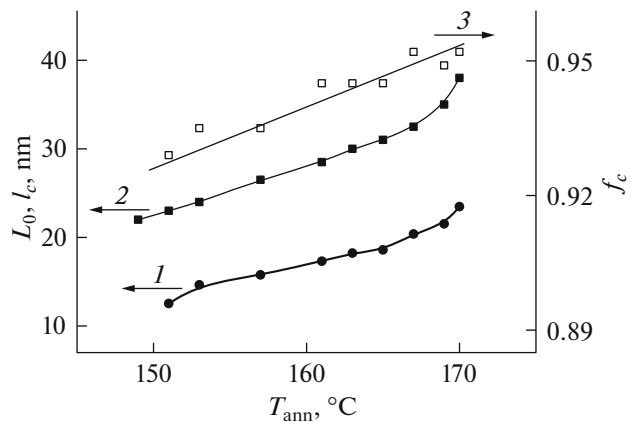


Fig. 1. Dependences of the structural characteristics ((1) the large X-ray period, L_0 ; (2) the thickness of lamellae, l_c ; and (3) the orientation factor, f_c) of the hard elastic samples on the annealing temperature.

Since the annealing was carried out with the fixed sample ends, i.e., the sample was under stress during crystallization, the process of structural rearrangement is accompanied by an increase in the orientation degree, which was characterized by the orientation factor f_c . As is seen from Fig. 1, the higher the annealing temperature, the more highly oriented structure is formed in hard elastic samples—the f_c value increases from 0.87 for extruded films to 0.95 for annealed ones.

The DSC data illustrate changes in the crystal structure of hard elastic films with varying the annealing temperature (Table 1). It is seen that an increase in the thickness of lamellae is accompanied by an increase in the melting temperature and enthalpy. It should be noted that the results obtained for an increase in the degree of crystallinity are in good agreement with the X-ray data given above.

The hard elastic properties of the annealed films are characterized by the following basic parameters: the value of the elastic recovery (ER_{100}) and the elastic modulus at extension. For flexible-chain polymers, the region of elastic deformations does not exceed 5–10%, as a rule. Being oriented, the initial extruded PP films had $ER_{100} = 48\%$. As can be seen from Table 2, the ER_{100} for the annealed films increases from 81 to 87% with an increase in the T_{ann} value; i.e., all the samples show a very high elastic deformability. The mechanical characteristics of the films at extension along the orientation direction and the direction perpendicular to it as a function of the T_{ann} value are given in Table 2. The data show that the elastic modulus in the direction of orientation increases with an increase in the T_{ann} value and reaches 2300 MPa, and the break elongation decreases, which is explained by an increase in the tension in the sample due to an increase in the tendency to shrink with an increase in the T_{ann}

Table 1. DSC data for hard elastic polypropylene samples

Annealing temperature, °C	Melting temperature, °C	Enthalpy of melting, J/g	Degree of crystallinity, %
149	165.8	97.5	59
155	166.4	98.2	60
161	168.0	101.4	62
165	169.1	103.4	63
170	171.0	104.7	64

Table 2. Mechanical properties of hard elastic PP films*

Annealing temperature, °C	Elastic recovery, ER_{100} , %	Strength, MPa	Elastic modulus, MPa	Elongation at break, %
149	81	81/27	1600/1450	400/2.5
155	82	80/28	1800/1480	360/2.5
161	83	80/28	2000/1520	320/2.5
165	85	79/29	2100/1540	300/2.5
170	87	79/29	2300/1570	270/2.5

*The values of the characteristics along the orientation direction are given in the numerator and along the direction perpendicular to the orientation direction are given in the denominator.

value and indicates an increase in the hard elasticity of the films. As was established in [11], the formation of such a structure possessing a combination of high values of the elastic modulus with the ability for large elastic recovery is a necessary condition for pores formation at the stage of uniaxial extension of hard elastic films.

The difference in the values of mechanical characteristics of hard elastic films along the orientation direction (\parallel) and in the direction perpendicular to the orientation direction (\perp) is a result of their oriented supramolecular structure. An increase in the E_{\parallel}/E_{\perp} ratio of the elastic moduli (Fig. 2) indicates an

increase in the anisotropy of the mechanical properties as a consequence of an increase in the degree of orientation of the films with an increase in the T_{ann} value. At the same time, the $\varepsilon_{\parallel}/\varepsilon_{\perp}$ ratio decreases with an increase in the T_{ann} value, because of a decrease in the ε_{\parallel} value at constant ε_{\perp} , which can be explained by the fact that a fixed force is applied to the sample in the orientation direction, and the structural rearrangement occurs mainly in this direction, without exerting a noticeable effect on the transverse ties between the crystallites.

3.2. Influence of the Annealing Temperature on the Structure of Porous Films

As was shown in [10–12], the extension of hard elastic samples, owing to their structural features is realized, according to the mechanism typical for the deformation of solids rather than to the entropy mechanism typical for amorphous-crystalline polymers, in which the stress is applied to the chains in the amorphous part. The load in this case is taken by the crystalline lamellae connected by rigid “bridges” (ties). The deformation of such a structure leads to the moving apart and bending of the lamellae between the points connected by ties, the break of some of the ties, and the pore appearance. It is clear that the properties of the obtained porous films depend on the characteristics of the hard elastic samples, which are controlled, as shown above, by the annealing temperature. The change in the structure of these samples with an increase in the T_{ann} value leads to an increase in the number and size of pores in the porous films and, as a

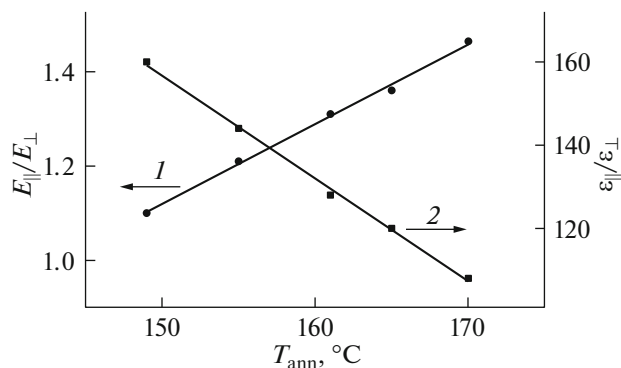


Fig. 2. Ratios between the values of (1) the elastic modulus and (2) the elongation at break along the orientation direction and along the direction perpendicular to the orientation direction for the hard elastic samples as functions of the annealing temperature.

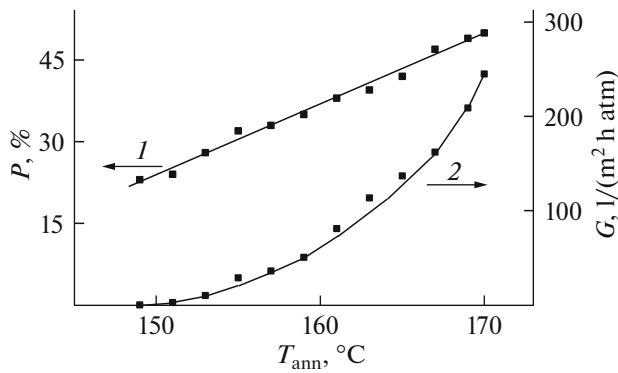


Fig. 3. Dependences of (1) the overall porosity, P , and (2) the permeability, G , on the annealing temperature for the porous films.

consequence, to their coalescence and the formation of through channels—the film becomes permeable for the flow of a liquid. The dependences of the overall porosity and permeability of the PP films on T_{ann} are shown in Fig. 3. As can be seen from Fig. 3, the overall porosity increases with an increase in the T_{ann} value in the whole range of its variation; at the same time, permeability (through channels) appears only when the annealing temperature during the preparation of hard elastic samples is above 149°C, i.e., the temperature, at which the threshold value is reached for the percolation parameter, the porosity, which is 23% for the PP films [17–19]. A further increase in T_{ann} gives rise to an increase in the permeability value of porous films. As is seen from Fig. 4, an increase in both the number and size of through pores contributes to an increase in the permeability value.

The DSC data (Table 3) show that the degree of crystallinity, and the melting temperature and enthalpy of the porous films increase with an increase in the annealing temperature; i.e., they change symmetrically with a change in these characteristics for hard elastic samples, but their values are somewhat lower in magnitude. This can be explained by the fact that the deformation of lamellae in the process of extension of the annealed films is accompanied by a split of a small number of crystallites, and their rotation and rearrangement with unfolding into ties. This is evidenced by some decrease in the orientation factor, f_c , from

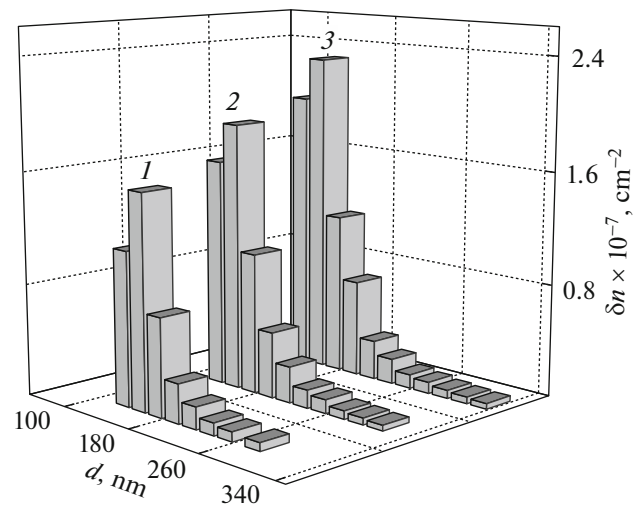


Fig. 4. Size distributions of through channels for the porous PP films obtained at various annealing temperatures of (1) 163, (2) 167, and (3) 170°C; d is the pore diameter; δn is the number of through pores in the range of sizes from d_i to d_{i+1} .

0.95 to 0.93 for annealed and porous samples, respectively.

The results of measuring the sound propagation velocity (v) for annealed and porous samples, depending on the propagation direction, are shown in Fig. 5. The higher sound propagation velocity in the porous sample in comparison with the annealed one (1.75 and 1.20 km/s, respectively), and also the ratios between the velocities along the orientation direction and the transverse direction ($v_{\parallel}/v_{\perp} = 1.5$ and 1.3, respectively) indicate an increase in the number of stressed crystalline ties in the porous film upon uniaxial extension.

Measurements of the mechanical characteristics of porous films showed that their strengths and elastic moduli reasonably decrease appropriate to an increase in the number and size of pores with an increase in the T_{ann} value. The deformation and bending of lamellae upon extension leads to a decrease in the elastic moduli of porous films in comparison with hard elastic samples both along the orientation direction and the direction perpendicular to it, that is the more noticeable at the higher T_{ann} (Table 4). However, the porous films are characterized by a higher ratio between the

Table 3. DSC data for porous polypropylene films

Annealing temperature, °C	Melting temperature, °C	Enthalpy of melting, J/g	Degree of crystallinity, %
149	163.3	86.3	52
155	165.1	89.4	54
161	166.2	95.0	58
165	167.1	97.8	59
170	168.7	98.8	60

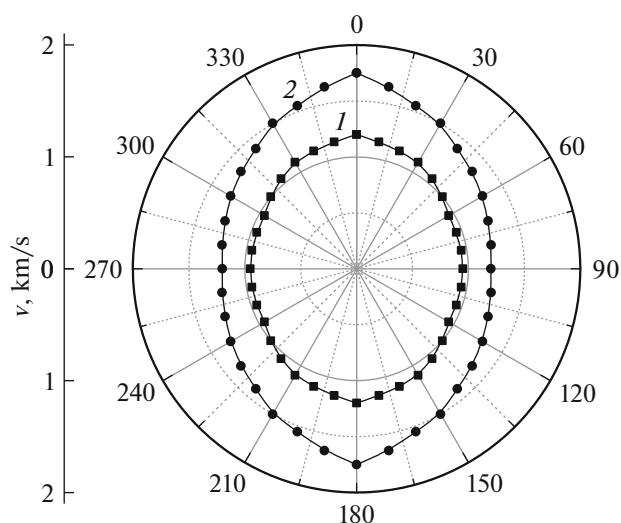


Fig. 5. Sound propagation speed in the (1) dense and (2) porous PP film samples.

elastic moduli in these directions, which indicates an increase in the anisotropy of mechanical properties as a result of extension. At the same time, the strength in the orientation direction, despite the appearance of defects (pores), for porous films is much higher than for annealed films, which is due to an increase in the number of stressed chains in the amorphous region under the influence of orientation forces arising in the process of extension of hard elastic films. However, these strength values decrease with an increase in T_{ann} as a result of an increase in the pore sizes and the break of a portion of stressed ties connecting the lamellae. These structural changes also manifest themselves in a significant decrease (by a factor of 5–6) in the break elongation in the orientation direction (Tables 2 and 4).

The pores formation also has a significant effect on the deformability of films in the direction perpendicular to the orientation direction that indicates the breaking of ties between the lamella stacks upon extension as a result of their displacement relative to each other. Thus, the strength along this direction in the porous films is 2.5 times lower than in the annealed

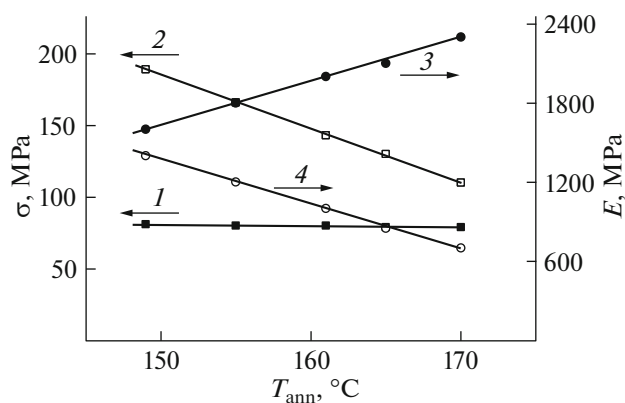


Fig. 6. Effect of the annealing temperature on (1, 2) the strength and (3, 4) the elastic modulus of the (1, 3) annealed and (2, 4) porous polypropylene films.

ones. This effect is also manifested in an increase in the elongation at break. Moreover, the deformation of the porous films along the direction perpendicular to the orientation direction follows the necking mechanism, which gave rise to a sharp increase in the measured ϵ_{\perp} from 100 to 200% with an increase in T_{ann} , as compared to ϵ_{\perp} for the annealed samples, which was 2.5% independently on T_{ann} (Table 2).

The given results make it possible to draw the following conclusions concerning the influence of the annealing temperature in the range from 150 to 170°C on the structure and properties of hard elastic and porous polypropylene films (Fig. 6):

(i) For hard elastic samples, an increase of T_{ann} leads to an increase in the thickness and the orientation degree of the crystalline lamellae, which manifests itself in an increase in the elastic modulus and a corresponding decrease in the elongation at break, but causes a decrease in the mechanical strength owing to a decrease in the number of tie chains involved in the crystallites, increasing their size;

(ii) For porous films, an increase of T_{ann} leads to an increase in the porosity and permeability, but the strength and elastic modulus decrease as a result of a decrease in the orientation degree when the lamellae

Table 4. Mechanical properties of hard elastic PP films*

Annealing temperature, °C	Strength, MPa	Elastic modulus, MPa	Elongation at break, %
149	189/11.3	1400/700	47/100
155	166/11.0	1200/620	47/140
161	143/10.8	1000/550	47/160
165	130/10.5	850/470	47/180
170	110/10.3	700/400	47/200

*The values of the characteristics along the orientation direction are given in the numerator and along the direction perpendicular to the orientation direction are given in the denominator.

move apart and bend in the process of pore formation. However, the strength of porous films is much higher than that of annealed ones, owing to an increase in the number of stressed chains under extension of hard elastic samples along the orientation direction.

CONCLUSIONS

The studies of the effect of annealing on the structure and characteristics of hard elastic and porous polypropylene films have shown that the annealing temperature is a basic parameter of the process of porous structure formation as for the functional (porosity, permeability, and pore size) as for mechanical properties, both, of these porous materials. The obtained results have made it possible to establish a mechanism of the structure transformation during the annealing and to reveal the dependence of the characteristics of porous films on the parameters of thermal treatment of hard elastic samples. The results of the studies lead to the conclusion that hard elastic samples should be annealed at temperatures close to the melting temperature of the polymer for the formation of high-permeability films and show that the porous films exhibit a high strength and maintain mechanical integrity, namely, they do not undergo fibrillization under loading in both directions. The obtained porous PP films possess high porosity and permeability that reach 50% and 245 l/(m² h atm), respectively, in combination with a high mechanical strength at a small thickness (about 17 μm), which makes it possible to consider them as promising membrane-separation materials characterized by low mass-transfer resistances.

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