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POROPHORS USED IN THE EXTRUSION PROCESS

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Abstract. The high density polyethylene (HDPE) modification by selected agents which are blowing agents during extrusion process, including the determination of modification effect on the selected physical properties and properties of the surface of HPDE extrusion products have been studied. The paper presents specification of the cellular extrusion process of thermoplastics with endothermic chemical blowing agents. The rotational speed of extruder, melt flow rate (MFR) and microscopic structure have been examined.

Keywords: thermoplastic polymer, cellular extrusion, blowing agent.

1. Introduction

Stream of the processed plastic material, together with the gas dissolved therein, is transported under pressure to the pre-forming head. The pressure should be high enough to prevent emission of gas as a separate phase (micro-bubbles) to the end of plasticizing system and extruder die. If this happened, membranes separating gas bubbles would suffer mechanical damage as a result of tangential stress occurring in the processed plastic material, and thus homogeneous cellular structure obtaining would not be possible. Plastic pressure increases along the plasticizing unit, slightly decreases in the terminal section of the system and at the front of the extruder head, and rapidly decreases inside the die reaching the value of atmospheric pressure.

1.1. Aspects of Cellular Extrusion

During the extrusion process, blowing agents undergo the same processing as the processed plastic, *i.e.* heating, compression, homogenizing treatment and carrying already before gas emission. Inert gases and low-boiling liquids may dissolve in the plasticized material, whereas porophor melting rate increases along with the increased mixing intensity and gas pressure. Proper process conditions are usually selected during the experiment.

Blowing agents used in the extrusion process can be divided into physical and chemical [1, 2, 6, 9], however this classification is traditional and not exactly accurate.

Physical blowing agents (physical porophors) include substances which do not change their chemical structure during the extrusion process; they only change their state of aggregation. Chemical blowing agents (chemical porophors) act like physical porophors, though gaseous products are the result of their decomposition and cause the cellular extrusion effect inside the plastic material.

Porophors used in the cellular extrusion of plastics may have exothermic or endothermic decomposition characteristics [1, 2, 4]. Porophors used to date usually have exothermic decomposition characteristics. In such a case, depending on conditions and extrusion method, it may be the cause of local overheating and as a result, the irregular cellular structure of the product. For the initiated exothermic porophor decomposition process automatically progresses even after energy cut-off. That is why products extruded with the use of such agents must be intensely cooled for a long time to prevent strains and keep the specific cellular structure. The main representatives of this group include hydrazides, *e.g.* sulfohydrazide and azocompounds, for instance azodicarbamide.

Blowing agents have endothermic decomposition characteristics; generation of gas during processing is rapidly stopped when the energy flow is cut off. Application of such blowing agents considerably shortens the cooling time. Examples belonging to this group include especially bicarbonates, *e.g.* sodium bicarbonate, ammonium bicarbonate and 2-hydroxypropanetricarboxylic acid [2, 6, 7, 9].

Different types of extruder heads are used in the cellular extrusion process. Straight mandrel, direct flow extruder heads for solid plastics are usually applied in order to obtain cellular products with small cross-sectional fields and thin walls. Channels in extruder heads of this type can be corrected relatively easy [4, 7, 9].

Cross-section of the extruder die should be reduced in relation to the cross-section of the cellular extrusion product. Section extruded in the die is a solid one and its volume increases only during free cellular extrusion at the moment of leaving the die and afterwards, when the Barus effect starts to overlap. Cross-sectional areas of extruder head channels should be relatively large to avoid considerable decrease in plastic material pressure and the die should be relatively short providing for large pressure decrease. Therefore, in cellular plastic extrusion, extruder dies with fixed section channels should not be used (sections which correspond to the sections of extruder product), which is common for heads used in extrusion of solid plastics [3, 6, 7].

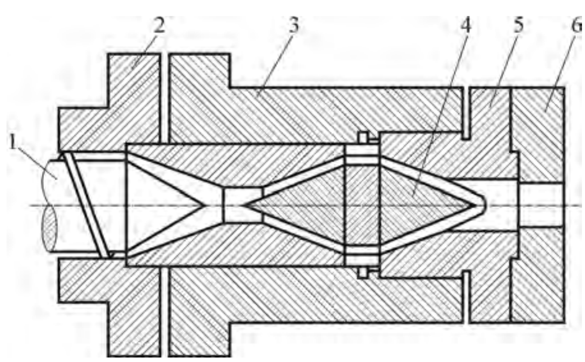

Fig. 1. Diagram of mandrel straight line extruder head with replaceable molding ring [4]: screw (1); extruder (2); head frame (3); core (4); sleeve (5) and exchangeable molding ring (6)

Another applied solution is provided by straight mandrel heads with replaceable moulding ring (Fig. 1). They contain modified standard mandrel heads. They are used during extrusion moulding of different types of shapes. Conoidal head mandrel enables generation of appropriate plastic pressure during cellular extrusion. By exchanging the moulding ring we can obtain the demanded shape and dimensions of extruder products.

In the cellular extrusion process, porous structure is formed by mixing the thermal decomposition products, chemical blowing agent with the material or inert gas brought in the system or directly formed. Blowing agents (porophors) is a source of gas which diffuses into the polymer and causes the pores. However, this does not mean that these additives must be in the form of gases, because chemical blowing agents are often porous solids or liquids, which release gaseous substances only during chemical reactions. For a porous material of appropriate structure and quality blowing agent has to be carefully selected, depending on process conditions, polymer type and the assumed parameters of the final product. The type and amount of added blowing agents have an effect on the final density of the porous material and determine the choice of porous method. In order to achieve a high degree of the mentioned method so-called physical blowing agents (gases, volatile liquids) are used. Chemical blowing agents are used where it is necessary to maintain low levels of capital expenditures on equipment and machinery. The essence of this process is the introduction of the plastic material (support): concentrated one (5–70 % concentration) or powders. The difference between the porous process of physical and chemical materials is that blowing agents are less associated with the course of the process, while the dosing of porophors to polymers is more important factor.

Physical blowing agents are placed under pressure in the system for plastic extrusion plasticizing. By adding a nucleaning agent you can get good separation of the physical blowing agent from plastic, and thus a uniform porous structure. They have many advantages and the main limitation is the ease of their concentration in the process. The fact that they generally require the use of special machines and processes can be regarded as a defect, but they are widely used in mass production of polystyrene and polyethylene foams. The physical blowing agents include, *inter alia*, nitrogen, carbon dioxide and air; the gas is dispersed in the polymer and expands, reaching atmospheric pressure. Unfortunately the use of air and nitrogen as additives of blowing agents requires special technological line mixer, in which these compounds are mixed with a liquid polymer such as latex. The blowing agent can use such volatile liquids as pentane or water added to the polymer in liquid form in order evaporation processing temperature cause pores. Due to their great tolerance to the part of the physical environment nitrogen and carbon dioxide are most commonly used as blowing agents.

Chemical blowing agents are substances decomposed in the plasticizing system and injected into mold cavity. They form gaseous substances resulting in porous materials. These agents may be added in the form of powders or as masterbach (premix) directly into granules or placed on the material in the production process. A mixture of plastic and blowing agents is processed in the plasticizing system (one or twinscrew), and then shaped in the mold. The heat brought in plasticizing system initiates the thermal decomposition of blowing agent and it is uniformly distributed in the home network of the polymer. The decomposition reaction produces mainly nitrogen, carbon dioxide and solid by-products. In this process the dissolved gas is obtained in the polymer, the same as in the case of physical blowing agents.

2. Experimental

Following the inspection of the extrusion process of cellular tape and examination of other structural cellular tape components, topcoat properties of cellular extrusion products were examined.

Modification of extrusion product and research on the extrusion process conducted in the Department of Polymer Processing at the Lublin University of Technology [4-6, 8, 9] are focused especially on the manufacture of products from cellular plastics, which results in the reduction of plastic purchase costs, energy costs of the process and transportation costs. At the same time, this results in the replacement of conventional extrusion process by the cellular extrusion process. The obtained extruder product may have a fully solid or cellular structure, it may be cellular in its entirety, or have a cellular core and a solid topcoat.

Extrusion of plastics, which involves the use of blowing agents, results in obtaining new modified physical and technological properties of extruder products [1, 3, 5-7]. They include reduced density of the product, minor shrinkage, enhanced noise suppressing and insulation properties, increased fire resistance, possible utilization after use. Inspection of selected physical, mechanical and usable properties of topcoats manufactured in the process of cellular plastics extrusion is a part of a larger research project.

The extruding process was carried out with the use of a single-screw extruder, type W-25 with the screw diameter D of 25 mm. The plasticizing unit was equipped with four heating zones. The process line consisted of the extrusion coating head, vacuum calibrator, the cooling bath and the remaining process line components.

HDPE manufactured by Lyondell Basell Industries, having a trade name Hostalen 4731 M, was used in the study of cellular extrusion process. This plastic has the density of 947 kg/m^3 and hardness of 59 Sh° D (according to data provided by the manufacturer).

Considering the nature of the conducted tape extrusion process temperature of the plastic in the plasticizing system and in the extruder head, plastic pressure and cooling conditions are among others. Blowing agents endothermically decomposed during the extrusion process should be used. In accordance with the established research program, plastic intended for extrusion was modified by introducing the blowing agent during the stirring process. In the present research a blowing system having a trade name of Hydrocerol CT 550, produced by Clariant Masterbatch Division was used. It is a blowing system with endothermic decomposition characteristics, taking the form of granules ranged from 1.4 to 1.5 mm in diameter. Hydrocerol CT 550 contains 70 % of the blowing agent mass with initial decomposition temperature of 423 K. The blowing agent is a mixture of sodium bicarbonate and 2-hydroxypropanoic-tricarboxylic acid (citric acid). In the present research Hydrocerol CT 550 was dispensed as 0.3–0.6 % of the mass.

The extrusion process was carried out under the developed and imposed conditions in the extrusion process line. Temperature values of heating zones in the plasticizing unit were respectively: 403, 433, 458 and 463 K; temperature in the extruder head for the three heating zones was 453 K. The determined rate of screw rotation was altered within the range of 0.83–1.25 s^{-1} (50–75 rev/min), whereas the receiving speed of the manufactured cable coating was 150 m/min. The temperature of the cooling agent was 290–293 K.

When using blowing agents of this type, it is important that porophor decomposition temperature exceed the mentioned one under proper processing conditions. In the cellular extrusion process, temperature of the extruder head should approximate decomposition temperature of the blowing agent. The degree of porosity of the product may be reduced or increased by regulation of the screw rotational speed.

Fig. 2. The appearance of the cabinet and the set of sensors used to read measurements of the cellular extrusion

3. Results and Discussion

Following cellular extrusion tests and certain physical properties of the manufactured cellular tape were examined. The article presents selected results of examination of density, degree of porosity, hardness, changing the rotational speed of the extruder, melt flow rate MFR and microscopic structure.

The density of the HDPE coating samples was determined using a pycnometric method. The measurements were made in conformity with the recommendations of the standard PN-EN ISO 1183-1:2006 *"Methods for determining the density of plastics"*. The measurements were made on samples coming from coatings with a mass in the range from 1 to 5 g. It has to be noted that because the cellular tapes were made of one solid layers and one foamed layer, which were impossible to unequivocally separate from one another during the density measurements, the calculated density of the HDPE cellular tapes samples is not the density of the foamed layer.

Table 1 shows the results of measurements of the normal density of cellular tape samples, the density of the cellular layer, and the degree of its porosity, obtained at various contents of the blowing agent.

Table 1

Apparent density, degree of coatings porosity and hardness of cellular tape modified by a blowing agent

Content of blowing agent, %	Degree of porosity, %	Density, kg/m^3	Hardness, Sh D
0	0	947	65
0.3	19	850	55
0.6	22	710	48

The relationship between density and degree of porosity *vs.* the amount of microcellular blowing agent is shown in Table 1. The microporosity of the plastic most effectively increases at microcellular blowing agent contents in the range of 0–0.3 %. This is confirmed by the fact that at the obtained degree of porosity of 19 % and density of 850 kg/m^3, the continuity of the cellular tape was maintained across its cross-section. In the case of the coating containing 0.3–0.6 % of the microcellular blowing agent, the degree of porosity of 19–22 % and the density of 710–850 kg/m^3 are satisfied. The wide scatter of cells in the coating may be due to uneven metering of such a low quantity of the agent.

The relationships presented here are partly brought out by the reviewed literature. The mechanical properties of modified HDPE, including its hardness, are affected by the shape and orientation of macromolecules and the bonds between them. Polymers with linear macromolecules and chains brought closer together as a result of crystallization or orientation, show higher strength than that of foamed polymers in which the action of intermolecular forces at the interface between the solid and gaseous phases is reduced.

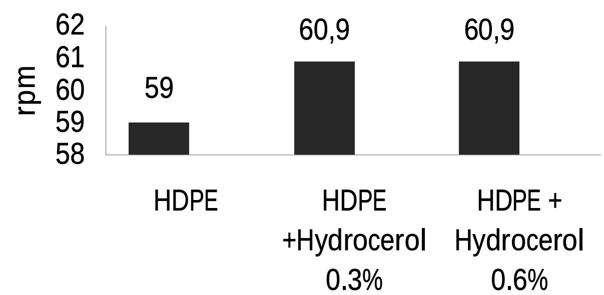

Fig. 3. The dependence of the changing the rotational speed of the extruder on blowing agent content in HDPE processing

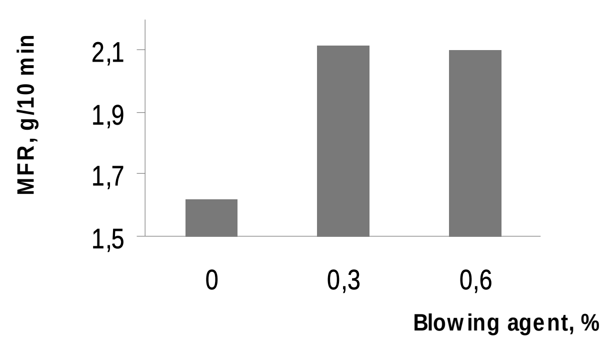

Fig. 4. The dependence of MFR on blowing agent content in HDPE processing

Analogously to the rotational speed of the extruder, the melt flow rate (MFR) increased monotonically and non-linearly over the entire range of increase in the content of the blowing agent. The largest increase in MFR, by an average of 30 %, occurred with a change in the content of the blowing agent in the range of 0–0.3 %; a further increase in the content of the blowing agent from 0.3 to 0.6 % caused an average increase of 7 %.

The mechanical strength of a polymer decreases with a decrease in the molecular weight from the moment until a balance is reached between intermolecular forces and the forces binding the individual atoms of the foamed-polymer chain. Mechanical strength is also affected by the shape and arrangement of macromolecules and the type of bonding between them. Polymers with linear macromolecules and chains brought closer together as a result of crystallization or orientation, show higher strength than foamed polymers, in which the intermolecular interaction forces are reduced. The lower number of transverse bonds in a foamed plastic decreases the strength properties of the product.

The results of the tensile strength tests, characterized by stress at break and relative elongation at break of modified-HDPE samples, are analogous to the results of hardness tests. Unfortunately, a foamed HDPE extrudate reduces mechanical properties, including its strength properties.

Microscopic studies of the cross-sections of the produced coatings structure were performed using an optical microscope. Based on the analysis of the obtained images (Figs. 5 and 6), it was found that the coating containing 0.3 % of the cellular blowing agent had a clearly visible solid outer skin and the most uniform distribution of micropores, all of which have the similar size. In the case of coatings containing 0.6 % of the blowing agent, the distribution was uneven and the pores visible were varied.

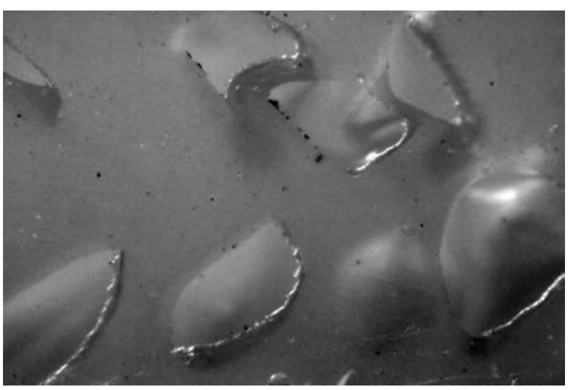

Fig. 5. Microscopic image of the cross section of the polymer made of cellular tape of the amount of the blowing agent (0.3 mas %; magnification of 50x)

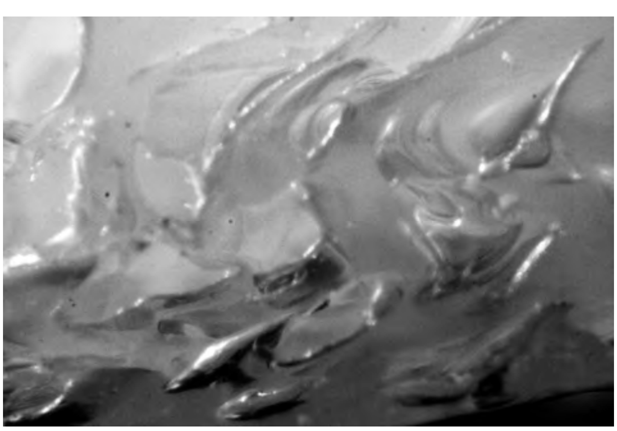

Fig. 6. Cross-sectional view of a cellular product with 0.6 % content of the blowing agent; magnification of 50x

Cellular extrusion consists in introducing into a polymer plastic a blowing agent, which decomposes with CO_2+N_2 gas emission under appropriate pressure and temperature conditions. This gas dissolves in the polymer. Next, after the pressure reduction the gas evolves from the polymer producing cellular structure, which has to be solidified by cooling the cellular product. If a solid layer is to be formed in the product, very intensive cooling has to be performed immediately after the polymer leaves the extrusion die. The cellular polymer at a certain distance from the die is not a stable system yet.

Exothermic porophors emit more energy during their decomposition than that required by this reaction. Once initiated, the decomposition spontaneously proceeds even after the source of energy has been cut off. That is why foamed products using this type of agents must be intensively cooled for a long time to prevent deformations. This may be the cause of local overheating and the formation of irregular cellular structure.

The main representatives of this group of agents are hydrazides, *e.g.* sulfohydrazide, and azocompounds, *e.g.*, azodicarbonamide. This latter compound is broadly used in the foaming of polyethylene, polyvinyl chloride, polystyrene and polyamide. In the case of blowing agents endothermic decomposition the gas evolution from the agent during processing abruptly ends as soon as the energy flow is cut off. The use of this type of blowing agents considerably shortens cooling time. This group is chiefly represented by bicarbonates, *e.g.*, sodium and ammonium bicarbonate and hydroxypropanetricarboxylic acid.

Compared with exothermic blowing agents, endothermic porophors considerably reduce product cooling time, thereby shorten the production cycle. Bicarbonates and citric acid are base materials for endothermic porophors. Because these substances are approved as food additives, their use is unproblematic.

4. Conclusions

Increasing content of the blowing agent, being a mixture of chemical compounds with endothermic decomposition characteristics, results in reduced density of the cellular product. Cellular products density is determined by the ratio of solid and gaseous phase, as well as the size and shape of microcells. As a result of increased temperature in the plasticizing unit and the extruder head, sodium bicarbonate and citric acid, comprising the blowing agent, undergo decomposition in a proper temperature. Numerous micro-bubbles formed due to pressure and surface development, immediately dissolve in the surrounding plastic. The formed microcells are filled in with air and gases, increasing the volume of polyethylene. The result is reduced density of the obtained cellular product.

Degree of porosity, being a property determining the volume of gaseous phase in the cellular product, at the same time determines the value by which the density of the product is reduced.

Mechanical properties, including tensile strength of the cellular product are affected by shape, orientation and macromolecule bonds. Smaller number of crosswise bonds in the cellular plastic results in reduced strength of the product.

Below we present important conclusions from the conducted examination of cellular cable coatings.

1. Manner of the blowing agent dispensing into the plastic used in the process was proved to be effective. No visual changes and no changed properties of the examined product have been observed, resulting from such manner of dispensing and mixing HDPE with the blowing agent Hydrocerl CT 550.

2. Quality of the obtained coating, taking into account such criteria as degree of porosity, density and other examined physical, mechanical and usable properties is assessed as very good. Density of the obtained coating was up to 710 kg/m^3 and its degree of porosity was up to 2 %.

3. The use of a blowing agent with endothermic decomposition characteristic from 0.3 to 0.6 % of the mass allows to obtain product meeting expectations and objectives of the conducted research.

Acknowledgments

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ПОРОФОРИ В ЕКСТРУЗИВНИХ ПРОЦЕСАХ

Анотація. *Вивчено модифікацію поліетилену високої густини (ПЕВГ) пороутворюючими агентами у екструзивному процесі. Встановлено вплив такої модифікації на селективні фізичні і поверхневі властивості отриманого ПЕВГ. Описано комірковий екструзивний процес термопластиків з ендотермічними хімічними пороутворюючими агентами. Встановлені обертальна швидкість екструдера, швидкості розтопленого потоку і мікроструктура модифікованого поліетилену.*

Ключові слова: *термопластичні полімери, комірковий екструдер, пороутворюючий агент.*