Modification with polymeric microspheres and its influence on thermal stability, mechanical properties and morphology of polyethylene

A Tor-Świątek

Department of Technology and Polymer Processing, Faculty of Mechanical Engineering, Lublin University of Technology, 36 Nadbystrzycka St., 20-618 Lublin, Poland

E-mail: a.tor@pollub.pl

Abstract. The structure modification of polymers has become essential due to a constant development of their applications, the necessity of changing or enhancing their functional and operational properties as well as higher product requirements. The aim of this study is to identify changes in the thermal, mechanical and structural properties. The article presents research results of low density polyethylene modification with a blowing agent in a form of polymeric microspheres. The temperature of extrudate during extrusion was regards to extrudate properties the morphology and mechanical analysis was carried out.

1. Introduction

The continuous development of the porous materials processing in the scope of the process and construction of machines, tools and devices included in the technological lines determines the enlargement of application areas for these materials. An important reason that causes the use of porous materials is the lowering of the products mass, both for complex or simple systems such as aircrafts, automobiles or packaging [1-3]. In most cases, the costs of manufacturing and their use are reduced. Due to their insulating properties, porous materials are used in construction and refrigeration [4]. They are good soundproofing agents, they can also be used to damp vibrations of machines. A higher interest in two-phase products has led to development of new processing methods such as cellular extrusion and cellular injection molding. A key factor here is the temperature of successive zones in the plasticizing unit. This parameter should be set such that the blowing agent undergoes decomposition in a suitable zone of the machine’s plasticizing unit. Another important factor is mixing efficiency which is determined by screw and barrel design [5].

The modification based on the addition of blowing agents involves the introduction of these materials during the processing or directly during their production. These products, decomposed during processing, by forming a mixture of a gaseous substance and a polymer. Porous agents used in the processing of polymeric materials may be in the form of gas, powder, granules, liquids and microspheres [6].

Microcellular blowing agent (porophor) is selected depending on the type of plastic, in the manner ensuring that its decomposition temperature is higher than the plastic melting point, but lower than the plastic extrusion temperature. Cellular plastic in liquid form is not yet a stable system because as a result of interfacial tension at the plastic – gas contact point, and as a result of diffusion, the number of
cells in the plastic is reduced, whereas their dimensions enlarge, which is an undesirable effect [7,8]. The obtained microcells continue to enlarge until gas pressure. Favourable structure of a small-cell plastic can be maintained in the product by its immediate cooling and solidification. Microcellular blowing agents used in the extrusion process can be divided into physical and chemical, however this classification is traditional and not exactly accurate [9]. Blowing agents used during microcellular extrusion of plastics may display exothermic or endothermic decomposition characteristics. Porophors used to date usually present exothermic decomposition characteristics. This may be the cause of local overheating and generation of irregular cellular structure of the product. The initiated porophor decomposition process progresses automatically even after energy cut-off. Therefore, products extruded with the use of such agents must be intensely cooled for a long time, in order to prevent strains and keep proper cellular structure [10,11].

As a result of separation of the porous structure, the products obtain new functional and technological properties, such as reducing the weight of the product, saving costs and materials, improvement of damping and insulating properties, reduction in processing shrinkage, increasing stiffness and reduction of flammability and water absorption [12].

Polymer microspheres belong to the new generation of porous agents, containing in their mass liquid hydrocarbon, which boils on the panes of elevated temperature and expands the polymer capsule.

The physical structure of porous products depends on the type of blowing agent used and its degradability and processing conditions and the polymer used [13,14]. To assess the physical structure, the basic geometric features of the pores should be determined, such as, for example, the pore counting ratio, the diameter and the pore distribution. The analysis of the physical structure can be carried out using the computer image analysis method, which allows quantitative and qualitative assessment of the size and distribution of pores in the cross-section of the porous product [15].

2. Experimental

2.1. Materials

LDPE was used, with the trade name Malen E FABS 23D022 (producer Basell Orlen Polyolefins) in the granulated form. The basic properties of the processed LDPE are shown in table 1.

| Property                  | Value |
|---------------------------|-------|
| Density, kg/m³            | 921   |
| MFI (190°C, 2.16 kg), g.10min | 2     |
| VST (A50, 10N), °C         | 91    |
| Hardnes Shore (D)         | 48    |
| Tensile strength, MPa     | 18    |
| Elongation at break, %    | 450   |

As a modifier the polymeric microspheres in the trade name Expancel 951 MB 120 (producer AkzoNobel) was used. Expancel microspheres occur in the form of spherical thermoplastic polymer capsules containing hydrocarbon gas (figure 1). Under the influence of heat, the capsule softens and the expanding hydrocarbon increases its volume, without damaging the very thin shell of the capsule. It is a medium with endothermic nature of decomposition. Spheres can not connect with each other because the capsules retain their barrier properties, which also effectively prevent the release of closed liquid. Expancel 951 MB 120 is a mixture that contains 65% microspheres in an ethylene / vinyl acetate (EVA) copolymer. Properties of microspheres are shown in table 2. The blowing agent in the form of polymeric microspheres was incorporated to LDPE as 0, 0.25, 0.5 and 1% wt.
Table 2. Selected properties of polymeric microspheres
Expancel used (producer data).

| Property                                         | Value     |
|--------------------------------------------------|-----------|
| Density with $T_{\text{max}}$, kg/m$^3$           | 12        |
| Temperature of starting expansion, °C             | 138-148   |
| Size, μm                                         | 28-38     |
| $T_{\text{max}}$, °C                             | 195-210   |
| Processing temperature, °C                        | 140-200   |

2.2. Processing
To investigate the polymeric microspheres modification effect on the thermomechanical properties and morphology of low-density polyethylene, the specimens were prepared by cellular extrusion process. The process was performed using a profile section extrusion line. This technological line consists of a single-screw extruder type T – 32 – 25 for extruding profiles and pipes. The parameters of the extrusion process was: temperature in plasticizing system zones 170, 180, 190, 200°C, temperature of extruder head 170°C, screw rotational speed 45 rpm, temperature of cooling factor 14°C. As a result, the microcellular extrudate was obtained in the form of a strip (figure 2).
The test program developed included measurements of thermal stability of extrudate during extrusion, tensile strength, elongation at break and morphology of extrudates.

The thermal stability was measured with the use of infrared camera V-20, in the section of extrudate including 29 points. Stimulus objects during the ongoing process of microcellular extrusion were nozzle of extruder head and the microporous extrudate leaving the nozzle head. Recorded the infrared radiation emitted by the surface of the examined objects, which after processing has enabled the visualization in the form of thermal images. A detailed analysis of temperature measurement was carried out on the along section of extrudate, which includes 29 points and across section of extrudate, which include 9 measuring points. The change in temperature during the extrusion process of the selected point on the surface of the extrudate at a distance of 40 mm from the nozzle was analyzed.

Measurements of mechanical quantities have been carried out on the Z 010 strength machine at a drawing speed of 50 mm/min. Type 1A specimens were previously excised according to EN ISO 527: 1998.

The morphology examination was performed on a test stand for microscopic examination consisting of an SEM microscope Nova NanoSem 450.

3. Results

The results of thermal stability of the LDPE extrudate during modification with microspheres were shown in figures 3-5.

With the increase of microspheres content, the temperature of the material leaving the nozzle of the extrusion head decreased, while in the tested dosing range it was a decrease of 10.04°C on average. In the tested dosing range, the extrudate temperature dropped uniformly along with the distance from the measuring head. At the same time, in the investigated range, the start of stabilization of the extrudate is visible from point 20 for a sample containing 1% microspheres.

Increasing the dispensing of the microcontroller influenced the cooling of the extrudate. Taking the reference value of the temperature drop in the solid extrudate measuring section (19.30°C), the 0.25% dosing resulted in a relative increase in the extrudate cooling rate by 34.5%, while the microspheres dosage of 0.5% resulted in an increase in the relative rate of extrudate cooling. 56.9%.

The tests of mechanical properties showed a significant effect of the microsphere contents on the tested values, i.e. Young's modulus, tensile strength and elongation at break. The results of individual parameters are shown in figures 6-8.

![Figure 3. Thermal image with section of extrudate measurements.](image-url)
Figure 4. Results of thermal measurements of extrudate temperature, measured along the extrudate section.

Figure 5. Results of thermal measurements of extrudate temperature, measured across the extrudate section.
Figure 6. Dependence of Young’s modulus on content of microspheres in LDPE extrudate.

Figure 7. Dependence of tensile strength on content of microspheres in LDPE extrudate.

Figure 8. Dependence of elongation on content of microspheres in LDPE extrudate.
Along with increasing the content of microspheres in LDPE, there was a significant decrease in all the mechanical properties tested. The largest decrease in Young's modulus is observed at the content of 0.25% of microspheres and it amounts to 30%, further increase of the content of microspheres by 0.5% and 1% causes further decrease of the modulus by 17% and 13% respectively. In the case of tensile strength also the largest decrease in this property is visible for sample 2 containing 0.25% of microspheres, increasing the content up to 0.5% resulted in a slight decrease in strength by about 4%, subsequent increase in the amount of microspheres in LDPE resulted in further reduction of strength by another 26%. Tested elongation at break shows a similar decrease of 65% of units elongation for samples containing 0.25 and 0.5% microspheres. The highest content of the agent is 1% wt. It caused a further significant decrease of this parameter by another 100% of elongation units.

Morphology studies of LDPE samples modified with microspheres are presented in figure 9. The analysis of the structure of the samples showed that due to the addition of microspheres to the plastic, its structure changes from solid to porous, containing pores of various sizes.

![Figure 9. Morphology of LDPE modified with microspheres in amount: A – 0%, B – 0.25%, C – 0.5%, D – 1%.

Along with increasing the content of microspheres in LDPE, the resulting pores are characterized by varying diameter and surface area. The pores B and C visible in figure 9 have a diameter in the range of 80 - 120 μm, and the pore diameter in figure 9D is in the range of 40 - 100 μm. It is worth emphasizing the fact that on the presented structures, there are visible pores, which are empty spaces, as well as whole microspheres with a clear border of the polymer coating, which is a protective layer of the active agent. This confirms the physical expansion of the microsphere under specific conditions without complete decomposition in the polymer matrix.
4. Conclusions
The present study shows that the content of the blowing agent in the form of microspheres significantly affects the thermomechanical properties and the morphology of low density polyethylene. The research found that the inserting of microspheres into LDPE significantly affect the bottom-thermal phenomena in the microcellular extrusion process, especially during the flow in channels and extruder head for cooling the extrudate directly in the extruder head. In the investigated range of microspheres content measure the temperature of extrudate leaving the extruder head attributed to endothermal effect accompanying expansion of the microspheres during the microcellular process. Moreover, we observed that the addition of microspheres significantly affects the mechanical properties of the product, weakening the extrudate by over 60% when dispensing the agent in an amount of 1% wt. in relation to the solid samples. This can greatly limit the applicability of this material. Analysis of the physical structure of the obtained marc used to verify the literature data suggesting complete plasticity of the microsphere in the material [5]. Studies have shown that the structure of the product remains full microspheres with significantly increased sizes, at the same time it should be treated as preliminary studies requiring expansion.

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