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Surface free energy of extruded polymer compositions

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Abstract: Suitable adhesive properties of the polymer compositions provide largely outer surface of the product. The aim of the studies was evaluation of the efficiency of the extrusion process and physical properties of PVC modified by selected auxiliary. In the studies PVC was used. PVC was modified by blowing agent (0-1.5% by mass) and antistatic agent (0-0.8% by mass) in the form of polyvinyl chloride concentrates. Efficiency of extrusion process is determined also by selected properties of surface layer of a mill cake of polyvinyl chloride. Surface free energy has been calculated in Owens-Wendt method. Antistatic agent causes diminishing of wettability and adsorption of surface layer and eventually increase of surface free energy of surface layer. For ensuring appropriate adhesion properties of a surface layer it would be advisable to use, for polyvinyl chloride modification, the antistatic agent in the amount not smaller than 0.4% by mass in relation to polyvinyl chloride mass. Taking into account research results, which can be useful during the development of processing technology of the polyvinyl chloride used for polymers composites, it can be stated that the content of the blowing agent used, noticeably decreasing polymer mass and simultaneously not worsening the properties of a surface layer, should not exceed 0.5-1.0% by mass in relation to polyvinyl chloride mass.

Keywords: extrusion process, blowing agent, antistatic agent, wettability, surface free energy, adhesive properties

1. Introduction

Suitable adhesive properties of the polymer compositions can be achieved using appropriate materials, and introducing plastic additives, which cause the modification, particularly effective in the area of the surface layer properties (Harding, 1997; Dalet et al., 1999; Bouhanks et al., 2016). Use of the polymer composition with a surface layer of reduced adsorption causes a reduction in the adhesion of impurities, particle foreign matter during transportation and handling. Modification of the polymer composition also relates to the manufacture of porous material, which will reduce the density of the material, and thereby the costs of its production (Żenkiewicz, 2000; Pocius, 2012; Myshkin et al., 2014).

However, PVC, because of considerably high surface resistivity shows a tendency towards static electrization, easily gathering the electrostatic charge on its surface, especially as a result of friction. This phenomenon is undesirable, contributes to dust deposition and other types of pollution on the product surface and can cause electric discharges.

Decreasing the friction resistance on the polymer composites surface can be obtained by modifying a surface layer of the composites through appropriate polymers and introduction into the polymer antistatic agents, which cause its modification, especially efficient in the scope of surface properties. The addition of antistatic agents into the polymers causes first of all the decrease of their polarity and surface resistivity (up to 10^6 ÷ 10^9 Ω), decreasing the gathering of the electrostatic charge on the polymer surface (Dalet et al., 1999; Zeng, 2013; Klepka et al., 2015; Nowak and Podsiadło, 2017).

Antistatic agents also reduce the polarity of the material, and as a result of limited miscibility with the material continuously migrate to the outer surface thereof, wherein in conjunction with atmospheric

moisture form the electroconductive coating (Klepka, 2001; Żenkiewicz, 2007; Czarnecka-Komorowska et al., 2018).

Surface free energy, which measures the state of a surface layer, is used during the estimation of the phenomena connected with adsorption, rewetting and adhesion. In the case of polymer products with a modified surface layer, in order to define free surface energy, a widely known method is used based on the measurements of wettability and rewetting angle (Della-Volpe et al., 1998; Garbacz, 2004; Pocius, 2012). Among many known ways of measuring the rewetting angle, a method of direct measurements of this angle by means of a goniometer is of great significance. The results of these measurements constitute the basis for computing surface free energy of polymers (Fig. 1).

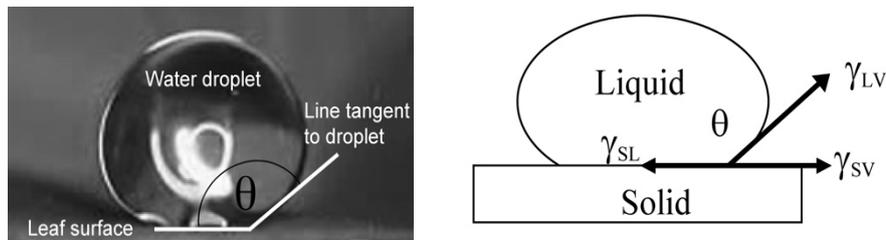


Fig. 1. The measuring principle for determining the contact angle (θ) and surface energy; γ_{SL} - surface energy solid/liquid, γ_{SV} - surface energy solid/vapour, γ_{LV} - surface energy liquid/vapour (www.intechopen.com, Courad et al., 2011)

The modification of the layer of the polymer composites also concerns the making of the layer from the blowing polymer, which causes the decrease of its weight, and through that, polymer purchase and transportation costs. Additionally, it results in simultaneously replacement of the conventional extrusion process with the blowing extrusion process (Garbacz, 2012; Tor-Świątek et al., 2016). A blowing agent (a porophor) can be gaseous, solid or liquid. Gases and liquids are introduced into the input polymer under appropriate conditions – under pressure, using special devices which deliver them to the feed section of the plasticating system during extrusion. Solids, on the other hand, as well as some liquids, are incorporated into the polymer already during its production. In the process of extrusion, porophors are subjected to the same laws of heating, compression, homogenization and transportation as the polymer being processed, even before the gas is released. Inert gases and low-boiling liquids may dissolve in the plasticated polymer, and their dissolution rate increases with an increase in mixing intensity and gas pressure (Palutkiewicz and Garbacz, 2016). This leads to the formation of a multi-zone porous layer with different cell numbers and sizes. The processing conditions for this process are usually chosen experimentally.

The similar literature reports only general or selected information, but rather of a inconclusive, concerning the modification of polymers using two additives at the same time: blowing agents and antistatic agents. There are no research results on the effectiveness of modification of the extrusion process characterized by changes in the sorption-diffusion properties (surface free energy) of the polymer compositions (Żenkiewicz, 2000; Pocius, 2012; Nowak and Podsiadło, 2017).

The aim of the conducted research was an assessment of the modifying effect of polyvinyl chloride with the selected agents (a blowing and an antistatic ones) on the course of the extrusion process, including the establishment of the influence of modification on selected physical properties and the surface properties of PVC extruded product. The further aim was the estimation of the analyzed polymer in regard to required conditions and properties of surface layers of the polymer composites.

2. Experimental

Based on the analysis of literature and taking into account the general conditions for experimental research methodology, a set of selected research factors characterizing the sorption-diffusion extrusion product, was chosen.

In the research programme, a rewetting angle θ (deg (rad)) of sample surface layer, was accepted as a directly studied factor, while the indirectly studied factor was free surface energy γ_s (mJ/m²). Antistatic agent was introduced into the PVC in the amount of 0 to 0.56% by mass. Blowing agent was

dosed in the range of 0 to 0.8% by mass. This results in the replacement of the conventional extrusion by the cellular extrusion process. The obtained extruded 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.

2.1. Materials

The tested material was PVC marketed under the trade name of Alfavinyl GMF/4-31TR, manufactured by Alfa PVC Sp. z o.o. (Poland). According to the data provided by the manufacturer, this plastic contains 31% plasticizer (dioctyl phthalate) and lime-zinc stabilizer. Its density $\rho_{(23\pm 2^\circ\text{C})}$ ranges from 1230 to 1400 kg/m³, the mass flow rate $\text{MFR}_{(150^\circ\text{C}/10,29\text{kg})}$ is between 4.3 and 4.6 g/10 min, the elongation at break amounts up to 300%, the tensile strength at break is ≥ 21 MPa and its Shore hardness A is equal to 80. The recommended processing temperature of this material is between 120 and 190°C.

Polyvinyl chloride was modified by auxiliary agents in the form of polyvinyl chloride concentrates. In the research presented in the article, a blowing system having a trade name of Hydrocerol PLV 751, produced by Clariant Group was used. Hydrocerol is a blowing system with endothermic decomposition characteristics, in the form of granules ranging from 1.5 to 1.6 mm in diameter, containing 70% of the mass of the blowing agent with initial decomposition temperature of 135°C. In the presented research, the blowing system was dispensed from 0.5% to 1.5% of the mass (0.14-0.56% blowing agent). The antistatic system was constituted by Lifostat 312 TPE dosed in the range of 2-8% (0.2-0.8 antistatic agent). The amount of antistatic agent in the system is 10% by mass. Lifostat 312 TPE is in the form of granules with a characteristic dimension (diameter) of the granules of 2.5 mm and a length of a grain 2.8 mm. This is an internal antistatic agent comprising a mixture of ethoxyamine tritanoloamine and glycerylmonostearate. TPE 312 Lifostat, distinguished by the fact that the action of antistatic agent occurs quickly, works for a long time and does not significantly affect the mechanical properties of the resulting materials.

2.2. Methods

The extruding process was carried out with the use of a single-screw extruder, type T-32-25 with the screw diameter of $D=32$ mm. The plasticizing unit was equipped with four heating zones. The process line was composed of the extrusion coating head, vacuum calibrator, the cooling bath and the remaining process line components. Section of a technological line is shown in Fig. 2. The extrusion process was conducted at the following parameters: screw rotational speed of 1 s⁻¹, temperature of heating zones of the plasticizing system of 120, 130, 140 and 150°C, respectively, temperature of the extruder head of 145°C.

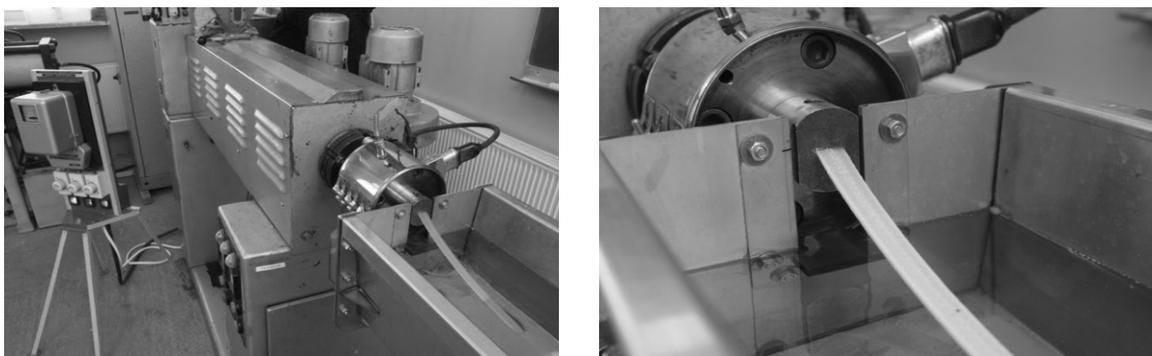


Fig. 2. View of technological line section for extrusion process

The extrusion head used during the tests is equipped with a heating zone of the assumed ring electric heater, sensor measurements of temperature and pressure, as well as the second temperature sensor - thermocouple. The head has a removable slotted nozzle to produce the tape. Width of the nozzle, used in the studies, is 22.00 mm and its height is 1.40 mm. In the study a removable, cooling system and exhaust belt, were used. Water cooling was also used in the research.

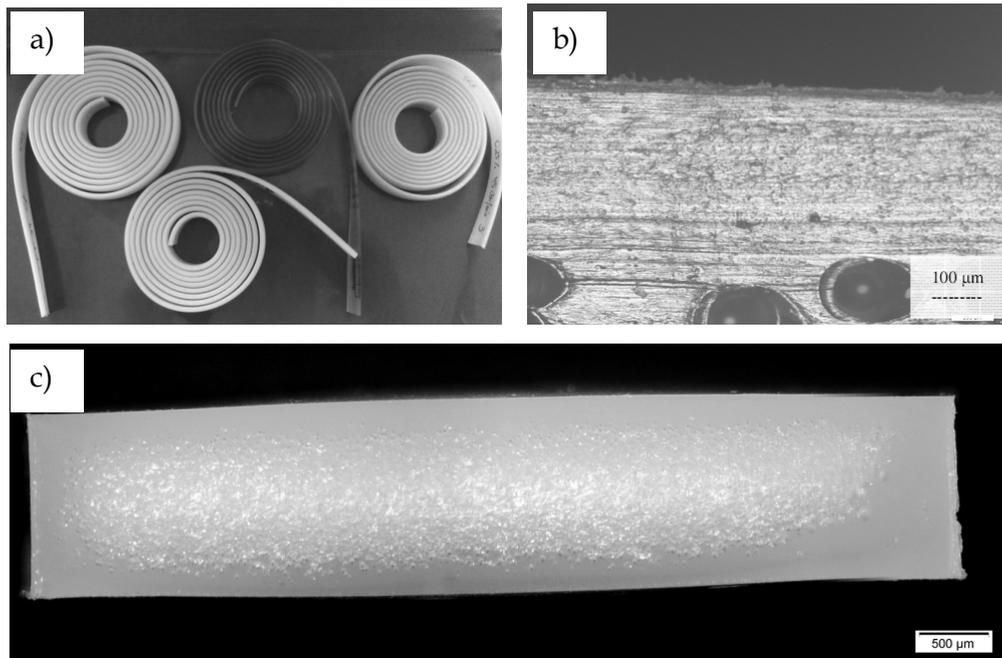


Fig. 3. Appearance of fragments generated from the PVC polymer compositions: (a) the appearance of the strip and the strip of porous solid, (b) the passage cross section of the PVC composition with visible wetted surface layer, (c) a cross-sectional sample of the polymer composition of PVC

Directly after the completion of the extrusion process, in which polyvinyl chloride extrusion products were received, the measurements of the rewetting angle were carried out. The measurements were conducted by means of a goniometer type PG-X produced by the Fibro Systems company (Fig. 4). Five measurement samples, measuring 10×60 mm, were cut from each extrudate. Then, by using a double-sided tape, samples were mounted on the goniometer measurement table, that was leveled and isolated from external vibration. Based on the analysis of the literature, consultations and preliminary examination, the measuring liquids and measuring droplet size were defined. For measurements of the rewetting angle, as an apolar fluid, a diiodomethan (CH_2I_2) was used, produced in the Loba company, and a polar fluid was glycerol. Basic research assumed a droplet volume of 3 mm for both fluids (ISO 8296). For each of the samples 10 drops of selected fluid were placed. Wetting measurements were made on both sides of the drop. As a result of the measurement value, the arithmetic mean of the two determinations was assumed.

On the basis of the literature analysis and conducted preliminary research, the Owens-Wendt method was used for the investigation of surface free energy of modified PVC (Żenkiewicz, 2000). This method is used in the study of surface free energy because plastic has a good theoretical justification and reproducibility of results obtained using different measuring liquids. This issue is particularly important where the modification process of the surface layer of the polymer compositions take place because the precise determination of the surface free energy is a prerequisite for the selection of modification process parameters.

In the method of Owens-Wendt, it is assumed that the surface free energy of the solid and liquid may be expressed as:

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (1)$$

where: γ_s^d component in the equation represents all the impact of a dispersion, γ_s^p and the component γ_s all polar interactions, as defined in the test method used.

When used set of measuring liquid, surface free energy was calculated by solving the system of equations using a special computer program.

$$\gamma_{lp} = \left(\frac{1 + \cos\theta_p}{2} \right) = (\gamma_s^d \cdot \gamma_{lp}^d)^{0.5} + (\gamma_s^p \cdot \gamma_{lp}^p)^{0.5} \quad (2)$$

$$\gamma_{ld} = \left(\frac{1 + \cos\theta_d}{2} \right) = (\gamma_s^d \cdot \gamma_{ld}^d)^{0.5} + (\gamma_s^p \cdot \gamma_{ld}^p)^{0.5} \quad (3)$$

where: γ_p , γ_p^d , γ_p^p – surface free energy and the polar liquid dispersion and polar component, respectively; γ_d , γ_d^d , γ_d^p – surface free energy of the dispersion liquid and its dispersion, as well as polar component, θ_p – the average value of the polar contact angle, θ_d – the average value of the contact angle of a liquid, γ_s^d , γ_s^p – dispersion and polar component of the surface free energy, respectively.

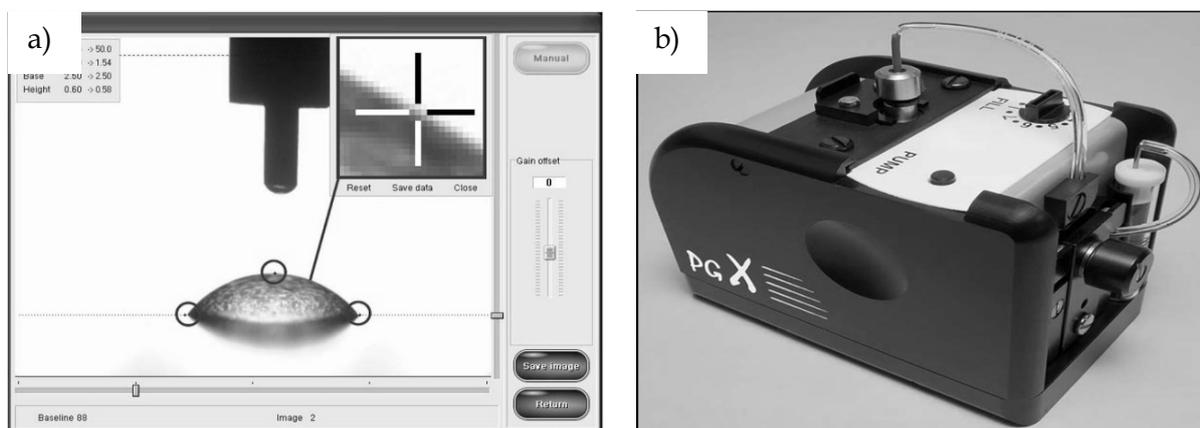


Fig. 4. View of the sample measurement screen (a) and goniometer PG-X (b) when determining the wettability of the surface of the polymer compositions

3. Results and discussion

The results of the measurements of wetting and surface free energy of the polymer compositions were summarized in Table 1. The table presents the arithmetic mean of the contact angle and the surface free energy, as well as standard deviation of the surface free energy.

The following table lists the columns in sequence: a – the content of blowing agent – BA (% mass), b – the content of antistatic agent – AA (% mass), c and d – the average contact angle θ_g glycerol and diiodomethane θ_d (deg), e – the polar component of the surface free energy γ_s^p (mJ/m²), f – dispersive component of the surface free energy γ_s^d (mJ/m²), g – the average value of the surface free energy γ_s (mJ/m²), h – the standard deviation of the arithmetic mean.

Table 1. Contact angles and surface free energy of surface layer of polymer composites at different content of antistatic and blowing agents

| BA (% mass) | AA (% mass) | θ_g (deg) | θ_d (deg) | γ_s^p (mJ/m ²) | γ_s^d (mJ/m ²) | γ_s (mJ/m ²) | S(γ_s) (mJ/m ²) |
|----------------|----------------|---------------------|---------------------|--------------------------------------|--------------------------------------|------------------------------------|---|
| a | b | c | d | e | f | g | h |
| 0 | 0 | 68.7 | 50.0 | 26.0 | 3.3 | 30.5 | 0.81 |
| 0 | 0.2 | 70.6 | 56.6 | 23.9 | 2.5 | 26.9 | 0.51 |
| 0 | 0.4 | 71.1 | 59.1 | 24.4 | 2.6 | 28.1 | 0.40 |
| 0 | 0.8 | 79.8 | 67.5 | 20.6 | 2.6 | 22.3 | 0.72 |
| 0.5 | 0 | 61.1 | 54.1 | 26.5 | 3.5 | 29.4 | 0.77 |
| 0.5 | 0.2 | 72.4 | 53.1 | 27.2 | 2.1 | 28.8 | 0.65 |
| 0.5 | 0.4 | 66.1 | 57.2 | 22.3 | 2.2 | 32.1 | 0.57 |
| 0.5 | 0.8 | 72.5 | 62.2 | 25.6 | 3.3 | 28.1 | 0.40 |
| 1.0 | 0 | 67.3 | 53.3 | 30.3 | 2.0 | 33.7 | 0.61 |
| 1.0 | 0.2 | 65.1 | 54.0 | 29.2 | 2.2 | 32.1 | 0.52 |
| 1.0 | 0.4 | 67.6 | 55.7 | 28.4 | 3.6 | 32.0 | 0.46 |
| 1.0 | 0.8 | 69.3 | 66.3 | 27.0 | 2.2 | 28.9 | 0.56 |
| 1.5 | 0 | 66.2 | 52.1 | 30.0 | 2.1 | 33.0 | 0.58 |
| 1.5 | 0.2 | 66.9 | 54.2 | 29.1 | 2.8 | 31.9 | 0.66 |
| 1.5 | 0.4 | 70.6 | 55.6 | 29.5 | 2.3 | 3.5 | 0.75 |
| 1.5 | 0.8 | 71.0 | 58.7 | 28.5 | 4.2 | 29.7 | 0.84 |

As a result of the measurements of the rewetting angle of a surface layer of the extruded product of unmodified polyvinyl chloride, an average value of this property was received. It equals 68.7° - when the research was conducted using glycerol, and 50.0° - when using diiodomethan. The received value of surface free energy of unmodified polyethylene equalled 30.5 mJ/m^2 , with the standard deviation of 0.81 mJ/m^2 . The value γ_s is approximate to the data presented in the literature (Żenkiewicz, 2000; Kovalev and Sturm, 2013). This confirms the correctness of the methodology used in the research. With an increase of antistatic agent content, in the range of $0 \div 0.8\%$ by mass, the rewetting angle increases. The scope of these changes depends simultaneously on the content of the blowing agent and the measuring fluid used during the research. The results of the measurements have the following values:

- $BA = 0\%$, $AA = 0 \div 0.8\%$; the rewetting angle changes in the range: glycerol $70^\circ \leq \Theta \leq 84^\circ$, diiodometan $50^\circ \leq \Theta \leq 70^\circ$,
- $BA = 0.5 \div 1.5\%$, $AA = 0 \div 0.8\%$; the rewetting angle changes respectively: glycerol $59^\circ \leq \Theta \leq 76^\circ$, diiodomethan $50 \leq \Theta \leq 70^\circ$.

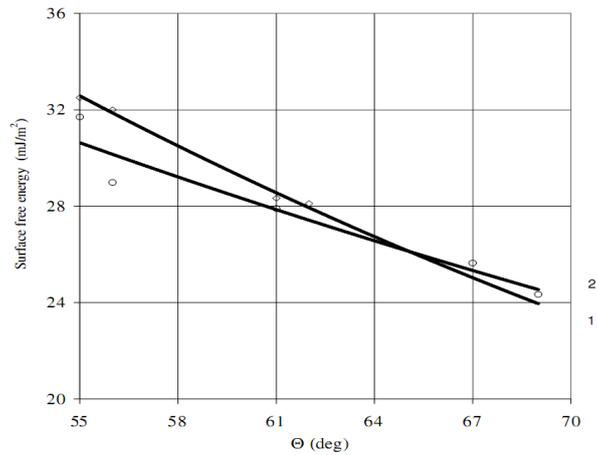


Fig. 5. The dependence of the surface free energy γ_s of surface layer of PVC composites from contact angle Θ :
1 - antistatic agent $AA = 0\%$, 2 - $AA = 0.8\%$, blowing agent $BA = 0 \div 1.5\%$

The received research results of free surface energy are presented in Fig. 5, whereas graphs of the dependence between free surface energy γ_s and the contents of auxiliary agents in modified polyethylene are depicted in Figs. 6 and 7. For the dependences described by the curves in Figure 5 it turns out that with an increase of the content of the antistatic agent in the whole studied range, the value γ_s decreases. The intensity of the decrease of γ_s is bigger at lower content of the $AA \leq 0.4\%$.

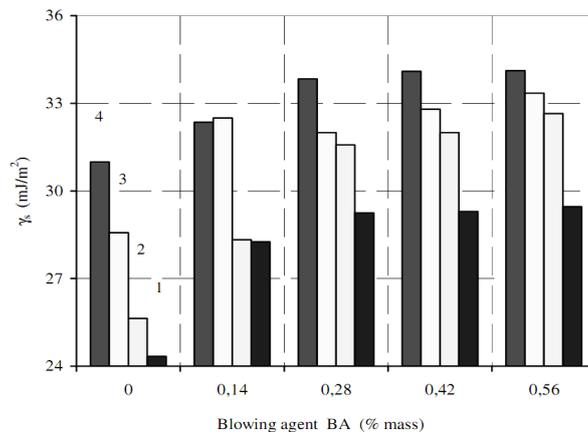


Fig. 6. The dependence of the surface free energy γ_s on the content of the antistatic agent AA in the polymer composites: 1 - antistatic agent $AA = 0\%$, 2 - $AA = 0.2\%$, 3 - $AA = 0.4\%$, 4 - $AA = 0.8\%$

With an increase of the content of the blowing agent (Fig. 6), the value of free surface energy increases and the course of these changes depends on the content of the antistatic agent. The intensity of the

increase of γ_s is bigger at lower values of the blowing agent $BA \leq 1.0\%$. For example, with the change of the value BA in the whole studied range at the content $AA = 0\%$, there is an increase of γ_s by 15%, from the value 31.3 to 36.2 mJ/m^2 . At the content $AA = 0.8\%$ and other variables as before, there is an increase of γ_s by 24%, from the value 23.9 to 31.1 mJ/m^2 .

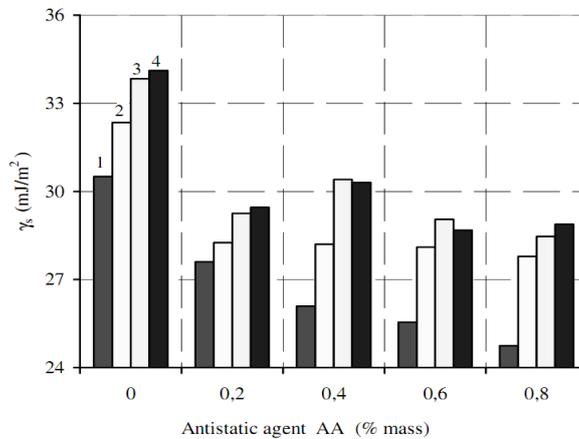


Fig. 7. The dependence of the surface free energy γ_s on the content of the blowing agent in the polymer composites: 1 - blowing agent $BA = 0\%$, 2 - $BA = 0.5\%$, 3 - $BA = 1.0\%$, 4 - $BA = 1.5\%$

4. Conclusions

The influence of the content of auxiliary agents used, on the rewetting angle of a surface layer of modified polyvinyl chloride extruded product was observed. The value of the rewetting angle decreases monotonically with an increase of the content of the blowing agent and increases in a comparable way with increasing content of the antistatic agent, in the whole range of dose of this agent. This is in accordance with the conditions of wettability of the solid body, where a big value of the rewetting angle indicates insufficient wettability and the decrease of free surface energy with increasing rewetting angle.

Free surface energy γ_s of a surface layer of modified polyvinyl chloride decreases monotonically in a non-linear way with the content of the antistatic agent, with additional simultaneous input of the amount of the blowing agent. The intensity of this decrease of γ_s is bigger at lower content of the antistatic agent, in the range up to 0.4% by mass. The conducted research confirms that the amount of adsorbed antistatic agent does not increase linearly, with an increase of its content in the polymer but more slowly when approaching the boundary value of saturation.

The increasing content of the blowing polyvinyl chloride agent causes an increase of the value of free surface energy of a surface layer of modified PVC polymer composition. The intensity of increase of the studied factor is bigger at the content of the blowing agent below 1.0% by mass, with additional change of the amount of the antistatic agent in the whole analysed range. This can be caused by increasing contact surface of adhesion with an increase of roughness of a surface layer. It constitutes a critical area of the polymer, inside which adsorption joints crack, which results in the wettability increase and, in consequence, an increase of surface energy.

Taking into account research results, which can be useful during the development of processing technology of the polyvinyl chloride used for polymers composites, it can be concluded that the content of the blowing agent used, which noticeably decreases polymer mass and simultaneously does not worsen essentially properties of a surface layer, should not exceed 0.5÷1.0% by mass in relation to polyvinyl chloride mass. For ensuring appropriate adhesion properties of a surface layer, for polyvinyl chloride modification, it would be advisable to use the antistatic agent in the amount not smaller than 0.4% by mass in relation to polyvinyl chloride mass.

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