Application of the Ozonation Process for Shaping the Energy Properties of the Surface Layer of Polymer Construction Materials

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ABSTRACT

The properties of the surface layer of construction materials are very important for making adhesive bonds. The article presents the test results for surface free energy in PA6 polyamide subjected to surface layer modification using the ozonation process. To develop the surface geometrically, the samples were subjected to mechanical processing. The comparison of results demonstrated that ozonation is an efficient and eco-friendly method of modifying the surface layer. The article also presents the comparison results for measurements of selected surface roughness parameters.

Keywords: surface layer, ozone, polymer materials, surface free energy

INTRODUCTION

To bond construction materials, among other things, the adhesive properties of adhesive substances are used. Therefore, proper preparation of the surface layer of bonded materials is so important [Kuczmaszewski 2006, Kłonica 2018, Laura et al. 2021]. Chemical methods, such as photolithographic etching of the polymer surface, radiation modification methods using UV or γ rays, or electron bombardment of the material surface, are examples of the multiple methods currently used for surface layer modification in polymer materials. However, the most promising method is ozone impact on the polymer surface. Due to the strong oxidising and radical-forming properties of ozone, this method could be used both in the plastics industry (in particular in biomedicine), construction, aviation, metallurgical and ceramics industry. Furthermore, compared to other polymer surface modification methods, ozonation is simple to apply, with low operating costs and no waste. Adhesion technologies are increasingly used as a method of construction bonding, in applicable machines and equipment operated under variable thermomechanical load

conditions. In adhesion technologies, the properties of the surface layer of construction materials are essential, including the surface free energy value [Kłonica et al. 2016, Bielawski et al. 2020]. The completed laboratory tests confirmed the efficiency of the method in increasing the surface free energy in the surface layer of PA6 polyamide, an important construction material for mechanical engineering.

Modification methods of the surface layer of polymers

The physical and chemical properties of "clean" polymers require modification to meet the operating requirements. It is best to modify the surface layer only, while leaving the properties of the internal structure of the polymer intact [Żenkiewicz 2000].

When analysing the reports in scientific literature, it is worth noting that a product called Synthetic Gecko was introduced to the market. It is a polyamide with a modified surface layer, resembling a gecko foot (hence the name). The surface of polyamide is coated with a thin layer of photosensitive emulsion, which is subjected to further

photolithographic processing. The polyamide modified in this manner by Davies and associates [Davies et al. 2009] is covered with millions of small mushroom-shaped trichomes that ensure adhesion by intermolecular interactions (van der Waals forces). In a similar manner, Geim and associates [Geim et al. 2003] produced polymer self-adhesive tape. The photolithographic process yields great results by improving the properties of the surface layer of polymers; however, it still involves different chemicals that generate waste that is difficult to treat.

An alternative to lithography is plasma application of anti-reflective coatings on a PMMA (polymethyl methacrylate) surface, which consists in ion etching. The surface with a structure resembling "insect eyes" is produced by bombardment, which causes a chemical reaction on it. The coatings with an "insect eyes" structure are not resistant to abrasion, so they are coated with a hydrophobic fluoroalkylsilane layer, which causes a super-hydrophobic effect on the surface, i.e. the coalescence of water drops that are removed from the surface with contaminants [Kaless et al. 2005].

Similar methods, such as "sol-gel" (of colloidal solutions) nano-coating application [Vamsi et al. 2021], micro-replication, which is based on holographic lithography, surface etching using argon with 4-hydroxyasobenzene and fluorinated alcohols [Milani et al. 2008], generate toxic substances in by-products and often require vacuum and increased temperature.

The use of ionising radiation enables the desirable modification of the properties of multiple polymers. Unlike photochemical phenomena, ionising radiation always interacts with all components of the material proportionally to their electron share. In most cases, the secondary effects of radiation are both crosslinking and degradation processes, which can be skilfully used to provide new properties to the polymer subjected to radiation processing. This method offers a significant improvement in the operating characteristics of materials, manifested in the increased resistance to abrasion, reduced moving resistance and surface polarisation, improved wettability and adhesion or increased thermal and chemical stability [Bieliński et al. 2006].

The impact of laser radiation photons results in lower energy emission than ionising radiation. However, it is sufficient to eliminate molecular and atomic hydrogen by cracking C-H bonds. In branched polymers, C-C bonds are cracked, which leads to the formation of oligomers. Laser radiation causes the formation of various free radicals, which initiate further reactions in this layer. An adverse phenomenon is the high increase of temperature generated by laser radiation, which may result in the polymer degradation process, in deeper material layers [Skurat 2003].

The most promising method seems to be the use of ozone generated in plasma reactors with barrier discharges [Okuda et al. 2007]. The surface layer of polymer materials is oxidised using ozone following the mechanism (1).
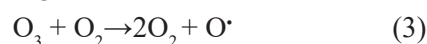
$$O_3 + P \rightarrow O_2 + PO \qquad (1)$$

where: P – polymer particle.

Ozone, which is characterised by high instability, is subject to decomposition:

$$O_3 \rightarrow O_2 + O^{\bullet} \qquad (2)$$

In addition, due to its highly oxidising character, the following reaction occurs:

$$O_3 + O_2 \rightarrow 2O_2 + O^{\bullet} \qquad (3)$$

In addition to ozone and O$^{\bullet}$, the reaction with the surface layer of the polymer involves other free radicals (e.g. $^{\bullet}$OH, $^{\bullet}$H), produced by ozone generation and its continuous reactivity, see equations (2) and (3) [Winands 2007]. Therefore, the products of these reactions include peroxide radicals, hydroperoxide groups, products of hydrogen peroxide decomposition and hydroxyl groups. However, the mechanisms and reactions occurring on the surface layer of polymers subjected to the impact of ozone and free radicals are not fully known at present.

As a result of oxidation of the surface layer of polymers, polar functional groups form on them, which significantly increase their wettability and the adhesive capabilities of the material. The presence of the mentioned functional groups is used, for example, in the metallisation process, in which the adhesion increase results from the formation of chemical bonds involving these groups and metal, e.g. aluminium [Ardelean et al. 2005].

The advantages of ozonation of the surface layer of polymer materials include the simple structure of reaction chambers, no waste and processing at atmospheric pressure and room temperature [Kłonica et al. 2019].

Physical and chemical properties of ozone and synthesis in low-temperature plasma environment

Ozone (O_3) is a three-atom particle with three atoms of oxygen. It is a gas with a distinctive odour. In the natural environment, ozone occurs in the stratosphere – the upper part of the atmosphere. In the stratosphere, ozone is generated by the collision of an oxygen particle and oxygen atom in the presence of neutral particle M (e.g. O_2, N_2) that intercepts the excess energy (4). Oxygen atoms are formed by the impact of UV radiation on the oxygen particle (5):

$$O^{\bullet} + O_2 + M = O_3 + M \qquad (4)$$

$$O_2 + h\nu = 2O^{\bullet} \qquad (5)$$
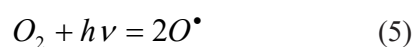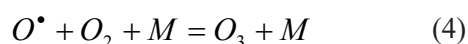
Ozone in the atmosphere acts as protective layer for the Earth, which absorbs UV-B and UV-C radiation. The maximum absorption occurs at the UV wavelength of 253.7 nm. The most important chemical properties of ozone include its remarkably high oxidising capability. The oxidation and reduction potential is E = 2.07 V. This gas is highly bactericidal (10 times more efficient than chlorine) and virucidal. Under "in vitro" conditions, ozone impact results in virion dissolution through reactions with unsaturated fatty acids in the lipid envelope of the virus. The ozone concentration safe for humans is 0.1 mg/m^3 [Bocci 2005].

Ozone is an unstable and quick-decomposition gas. An increase of temperature and humidity accelerates the decomposition process. At room temperature and low relative humidity of air, ozone decomposes after approx. 20 minutes [Winands 2007].

At present, ozone is produced on a laboratory and technical scale primarily in plasma reactors with barrier charges. Barrier discharges are silent (incomplete charges). Ozone synthesis follows the reaction (6).

$$3O_2 \rightarrow 2O_3,$$
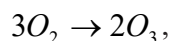
$$\Delta H = 144.4 \text{ kJ/mol}, \Delta G = 165.0 \text{ kJ/mol} \qquad (6)$$

The process is strongly endothermic (high reaction enthalpy ΔH) and occurs with an increase of free enthalpy ΔG, which indicates the requirement to feed a lot of energy to the system. The reaction is irreversible, and its efficiency decreases as temperature increases. The positive value ΔH indicates that ozone is unstable [Ozonek et al. 2007].
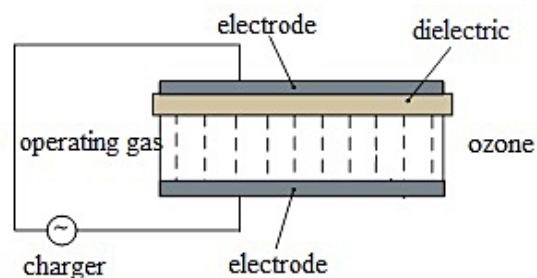

Fig. 1. Diagram of ozone generator with barrier chargers

Figure 1 shows the design of a typical plasma reactor with barrier (silent) charges. This type of reactor is the most "mature" technologically and the industrial plants used to generate ozone exceed the capacity of several hundred kW. An advantage of such a reactor is that electrodes are installed outside the reaction zone. This eliminates multiple problems with electrode erosion and contamination. The electrodes are supplied with alternating current voltage. In the analysis of the ozone generation mechanism, the course of primary processes in the ozoniser gap must be considered. The electrical current flowing from the gap is primarily conducted by electrons. This gap is a discharge area that consists of a large number of micro-charge "ducts", also referred to as streamers ("life" time ~10^{-6} s).

In a barrier charge, the average electron energy is several eV. The advantages of this type of discharge are operation at atmospheric pressure, low temperature of the work gas (300–400 K), discharge parameters independent of the composition of gas subject to processing and simple production. The disadvantages of the reactors with barrier discharges are the small distance between electrodes (up to 5 mm) and the related small working area of the reactor [Kogelschatz 2000].

Surface free energy

The parameter that determines the efficiency of bonding of polymer surfaces is adhesion energy, which is the work necessary to separate two layers of bonded material, regardless of the type of interactions resulting in the formation of a fixed bond.

The balance of the surface and interfacial free energy in the solid-liquid-gas system is described by Young's equation (7), the graphic interpretation of which is presented in Figure 2:
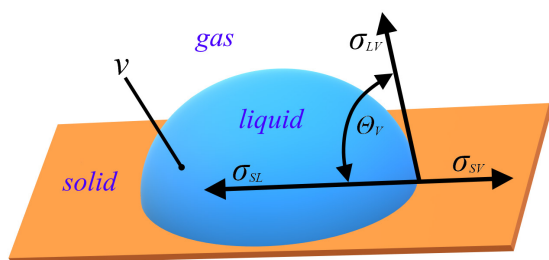
Fig. 2. Graphic interpretation of Young's equation

$$\gamma_S = \gamma_L \cos \theta + \gamma_{SL} \qquad (7)$$

where: γ_S – surface free energy of the solid,
γ_L – surface tension of the liquid,
γ_{SL} – solid-liquid interfacial free energy,
θ – wetting angle.

Based on the definition of the solid-liquid interface energy:

$$\gamma_{SL} = \gamma_S + \gamma_L - W_A \qquad (8)$$

where: W_A is the work of liquid to solid adhesion; after input of equation (8) to equation (7), the expression of adhesion work W_A is obtained, when the solid surface is not coated with liquid film, under wetting angle measurement conditions [Chibowski et al. 1993].

$$W_A = \gamma_L \left(1 + \cos \theta \right) \qquad (9)$$

Experimental, and even more theoretical, determination of the surface free energy in solids is still difficult and entails multiple theoretical and experimental problems. The most commonly used method is the measurement of the wetting angle of the testing liquid on a flat surface [Chibowski 2007].

According to Fowkes [Fowkes 1964], for a solid-liquid system, in which the dispersion interactions are decisive, the value γ_{SL} in Young's equation can be expressed by the geometrical average of the dispersion components of the liquid and solid surface free energy:

$$\gamma_L \left(1 + \cos \theta \right) = 2 \left(\gamma_S^d \gamma_L^d \right)^{1/2} - \pi_e \qquad (10)$$

where: γ_S^d – dispersion component of surface free energy of the solid,
γ_L^d – dispersion component of the surface tension of the liquid,
π_e – liquid film.

For high energy liquids in contact with low energy solids, the surface energy of which results from dispersion interactions, it can be assumed that $\pi_e = 0$, because the high energy liquid film

cannot lower the surface free energy of the low energy solid [Fowkes 1964]. For $\gamma_L > \gamma_S$, we will obtain:

$$\cos \theta = -1 + 2 \left(\gamma_L^d \right)^{1/2} \left(\frac{\gamma_L^d}{\gamma_L} \right)^{1/2} \qquad (11)$$

Owens and Wendt [1969], by extending Fowkes theory, assumed that if polar interactions (non-dispersive) occur at the interface, then Young's equation enables determining the dispersion (γ_S^d) and polar (γ_S^p) component of free surface energy of the solid after expression γ_{SL} in the function of the geometrical average of these components:

$$\gamma_L \left(1 + \cos \theta \right) = 2 \left(\gamma_S^d \gamma_L^d \right)^{1/2} + 2 \left(\gamma_S^p \gamma_L^p \right)^{1/2} - \pi_e \qquad (12)$$

Based on the measured wetting angles of two liquids (e.g. water and diiodomethane) with known γ_L^d and γ_L^p component values, after solving two equations (12) and assuming that $\pi_e \cong 0$, γ_S^d and γ_S^p can be calculated for the solid.

The Owens-Wendt method is the most popular method of determining the surface free energy of polymer materials [Żenkiewicz 2007].

MATERIAL AND METHODS

The samples are made of PA6 polyamide, with the dimensions of 100×25 mm and thickness of 3 mm. Before determining the surface free energy, the geometrical surface was also "developed" using the cover tool with P320 grit. For comparison purposes, the surface was also developed by sandblasting. For the measurement of the wetting angle, distilled water and diiodomethane were used as test liquids. The following constant values of the surface free energy of test liquids and their polar and dispersion components were assumed: $\gamma_w = 72.8$ mJ/m^2, $\gamma_w^p = 51.0$ mJ/m^2, $\gamma_w^d = 21.8$ mJ/m^2, $\gamma_d = 50.8$ mJ/m^2, $\gamma_d^p = 2.3$ mJ/m^2, $\gamma_d^d = 48.5$ mJ/m^2.

The surface free energy in test samples was determined on geometrically developed surfaces, then the samples were subjected to modification of the surface layer in ozone atmosphere with different conditioning times. After the ozonation of samples, the wetting angles necessary to determine the free surface energy were measured again. The measurement of the wetting angle with distilled water and diiodomethane was made at

least seven times for every sample. For the measurement of wetting angles, a PGX goniometer with automatic feeding of test liquids was used. For the measurement of selected parameters of 2D surface roughness, the 3D contour, roughness and topography measurement device T8000 RC-120-400 by Hommel-Etamic with measuring tip with 2 µm radius was used. The results were analysed using TURBO WAVE software. Figure 3 is a schematic presentation of the laboratory station for ozone synthesis and PA6 polyamide surface layer modification. The tested samples are placed in a glass reaction chamber. Figure 4 shows the construction materials ozonation station.

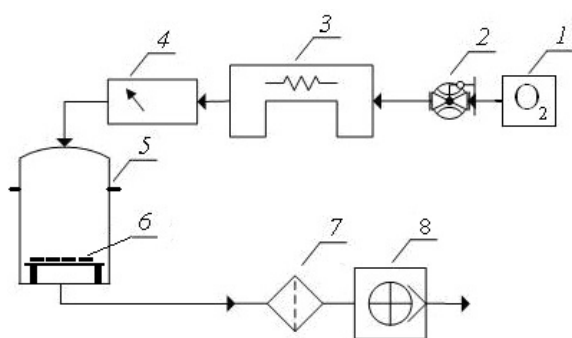The flow of ozone during sample ozonation is 0.90 dm³/min. The concentration of ozone is

Fig. 3. Construction material samples ozonation station layout: 1 – oxygen concentrator, 2 – adjustable flowmeter, 3 – ozone generator, 4 – ozone concentration meter, 5 – reaction chamber, 6 – samples subjected to surface layer modifications, 7 – ozone destructor, 8 – suction pump

7 g/m³. Ozone concentration was measured using the ozone meter Ozone ANALYZER BMT 964. The samples were conditioned in the reaction chamber for (5, 20 and 30) minutes, as appropriate. The surface free energy tests were carried out on five samples for each ozonation time.

RESULTS

Figure 5 presents the selected profiles of the 2D surface roughness of PA6 polyamide after mechanical modification of the surface layer, i.e. after roughening and after sandblasting. After the ozonation of mechanically processed samples, no significant changes in surface roughness profiles were found. The results for the selected surface roughness parameters are listed in Table 1. Ten measurements were made on each sample surface.

Based on the tests, it is worth noting that both processing with a cover tool with P320 grit and sandblasting are efficient in geometrical surface development and provide good conditions for adhesion technologies. Furthermore, it is worth mentioning the efficient cleaning and removal of the layer of contaminants formed in the production process. Figures 6 and 7 show the test results of the energy condition of PA6 polyamide after different preparation and modification methods. Figure 6 shows the surface free energy (SFE) of PA6 polyamide after roughing and modification in ozone atmosphere.

Based on the tests, the surface free energy of PA6 polyamide was found to increase after

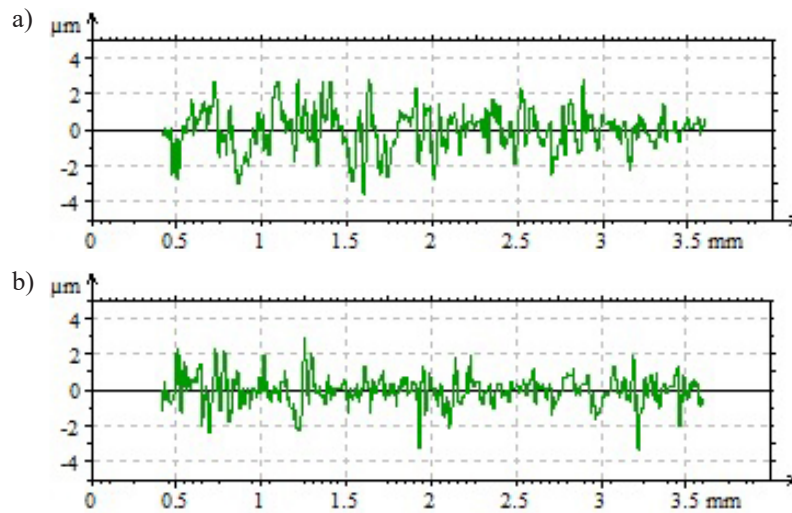**Fig. 4.** Construction materials ozonation station

Fig. 5. The selected surface roughness profiles of PA6 polyamide:
a) after roughing, b) after sandblasting

ozonation compared to the samples before ozonation. The largest increase was found in samples after ozonation for 30 minutes. Compared to the samples before ozonation, this increase was approx. 12%. Figure 7 shows the surface free energy (SFE) of PA6 polyamide after sandblasting and modification in ozone atmosphere.

In samples made of PA6 polyamide subjected to sandblasting and ozonation, the surface free energy was also found to increase compared to the samples subjected to sandblasting before ozonation. The smallest increase of the surface free energy was found in samples after ozonation for 5 minutes. Compared to the samples before ozonation, this increase was

approx. 5%. However, the highest SFE increase was found in samples subjected to ozonation for 30 minutes, compared to samples before ozonation, with it being 11%.

CONCLUSIONS

Based on the completed tests of energy properties of the surface layer of PA6 polyamide after ozonation, the following conclusions may be formulated. For PA6 polyamide, ozonation causes an increase of the surface free energy value, estimated at approx. 5% for the conditioning time of 5 minutes and approx. 12%
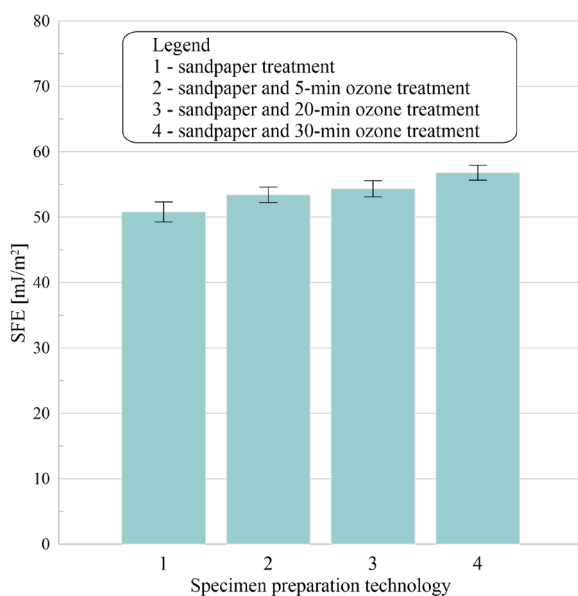

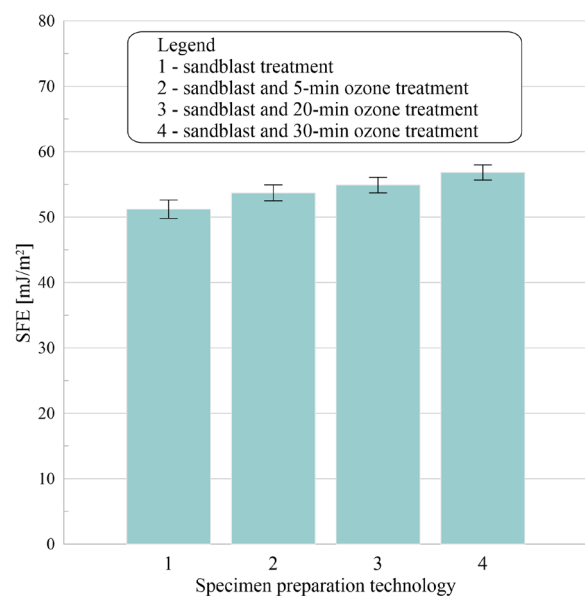**Fig. 6.** Free surface energy of PA6 polyamide after roughing and ozonation

Fig. 7. Free surface energy of PA6 polyamide after sandblasting and ozonation

for the conditioning time of 30 minutes. Based on the completed tests, significant differences were not found in the values of the selected parameters of surface roughness for PA6 polyamide after ozonation, compared to samples before ozonation. Considering the highly "disinfecting" properties of ozone, it should be assumed that even a small increase in the surface free energy value could be significant for the long-term strength of adhesion bonds of PA6 polyamide (in the context of PA6 polyamide ageing under bacterial impact). Ozonation can be a promising alternative to the so-called "wet chemicals" in the energy activation process of the surface layer of polymer materials.

Acknowledgements

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