KATARZYNA POJNAR[1, 2, *]
ORCID: 0000-0001-9877-7448

BARBARA PILCH-PITERA[1]
ORCID: 0000-0002-2412-2219

NATALIA ROŚ[1]

ŁUKASZ FLORCZAK[3]
ORCID: 0000-0003-3368-275X

[1] Rzeszow University of Technology, Faculty of Chemistry, Department of Polymers and Biopolymers, Rzeszów, Poland

[2] Doctoral School of Engineering and Technical Sciences, Rzeszow University of Technology, Rzeszów, Poland

[3] Rzeszow University of Technology, Faculty of Chemistry, Department of Physical Chemistry, Rzeszów, Poland

* Corresponding author

Low-temperature powder paint modified with graphene oxide

Niskotemperaturowe lakiery proszkowe modyfikowane tlenkiem grafenu

The aim of this study was to obtain low temperature polyurethane powder paint based on a thermosetting acrylic resin modified with graphene oxide (GO) and to investigate the protective properties of the coatings. The acrylic resin was synthesised by the radical copolymerisation reaction of 2-hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA) and n-butyl acrylate (BA). Graphene oxide was added to the resin at the synthesis stage in appropriate amounts by weight (so-called in situ method). An optimal amount of added graphene oxide of 0.5 wt% had a significant effect on the final result. Thanks to the use of a commercial crosslinker (VESTANAT B 1358/100), the coatings cured at a relatively low temperature (160℃). The curing process of the coatings was studied by differential scanning calorimetry (DSC). The cross-linked coatings were examined for appearance, physical and chemical properties, and resistance to corrosive media by electrochemical impedance spectroscopy (EIS). The presence of a modifier in the form of graphene oxide increased the hardness, scratch resistance, ductility, contact angle and resistance to corrosive media of the coatings obtained.

Keywords: powder coatings, graphene oxide, anti-corrosion properties

Celem badań opisanych w artykule było otrzymanie niskotemperaturowych poliuretanowych powłok proszkowych na bazie termoutwardzalnej żywicy akrylowej modyfikowanej tlenkiem grafenu (GO) oraz określenie właściwości ochronnych powłok. Żywica akrylowa została zsyntezowana w reakcji kopolimeryzacji wolnorodnikowej metakrylanu 2-hydroksyetylu (HEMA), metakrylanu metylu (MMA) i akrylanu n-butylu (BA). Tlenek grafenu został dodany do żywicy na etapie syntezy w odpowiednich ilościach wagowych (metodą in situ). Istotny wpływ na wynik końcowy miała optymalna ilość dodanego tlenku grafenu – na poziomie 0,5% wag. Dzięki zastosowaniu komercyjnego środka sieciującego VESTANAT B 1358/100 powłoki utwardzały się w stosunkowo niskiej temperaturze (160℃). Przebieg procesu utwardzania powłok badano za pomocą różnicowej kalorymetrii skaningowej (DSC). Usieciowane powłoki analizowano pod kątem wyglądu, właściwości fizykochemicznych oraz odporności na media korozyjne, wykonując pomiar metodą elektrochemicznej spektroskopii impedancyjnej (EIS). Obecność modyfikatora w postaci tlenku grafenu zwiększyła twardość, odporność na zarysowanie, tłoczność, kąt zwilżania oraz odporność na media korozyjne otrzymanych powłok.

Słowa kluczowe: lakiery proszkowe, tlenek grafenu, właściwości antykorozyjne

Mgr inż. Katarzyna Pojnar graduated from the Faculty of Chemistry, Rzeszow University of Technology in 2020. She is a PhD student in the Department of Polymers and Biopolymers of this university. Research topics: research on the powder coatings based on acrylic resins.
E-mail: d521@stud.prz.edu.pl

Dr. hab. Barbara Pilch-Pitera, Professor at the Rzeszow University of Technology, is an employee of the Department of Polymers and Biopolymers of the Faculty of Chemistry. Research topic: polymers, plastics, paints, lacquer, polymer coatings.
E-mail: barbpi@prz.edu.pl

Mgr inż. Natalia Roś graduated from the Faculty of Chemistry, Rzeszow University of Technology in 2023. Specialty: organic technology and plastics.
E-mail: nataliaros98@wp.pl

Dr. inż. Łukasz Florczak graduated from the Faculty of Chemistry at the Rzeszow University of Technology in 2012. In 2018, he obtained a PhD in chemical sciences at the same faculty. Currently, he works at the Department of Physical Chemistry at the Faculty of Chemistry of the Rzeszow University of Technology. Specialty: applied electrochemistry.
E-mail: l.florczak@prz.edu.pl

1. Introduction

One of the key directions in technological development is ecology. Unlike traditional paints based on organic solvents, powder coatings do not contain any volatile organic compounds (VOCs), which means that there are no emissions during the curing process that cause air pollution [1]. Another very important consideration is energy efficiency. The powder coating process minimises material and energy wastage [2]. The absence of solvents in powder coatings means that there is no loss of material caused by evaporation during the drying process. In addition, when powder is sprayed onto a substrate, particles that do not adhere to the painted surface can be collected by a cyclone and reused, which helps to reduce waste and minimise material loss. Low-temperature or UV-curable powder coatings [3] are also becoming more common. These technologies consume significantly less energy than standard high-temperature technologies (curing temperatures above 160°C) and allow powder coatings to be used not only on metal but also on heat-sensitive materials [4].

Due to the many advantages of powder coatings over traditional solvent-based paints, they are increasingly being used in various industries, and provide durable, aesthetic and more environmentally friendly finishes. Due to the wide range of resins, curing agents and additives available and used to impart specific properties, powder coatings are used to protect metals from corrosion in the automotive, construction, machinery, domestic appliance, furniture and electronics industries, to name a few [5].

Corrosion of metals is a serious problem that results in enormous economic loss. In order to protect metals from this process, various techniques are used to protect their surfaces, such as electroplating, anodising and the application of organic protective coatings. The application of organic coatings is one of the most widely used methods of protecting metals against corrosion because as is the most economical and versatile [6]. The ability of organic coatings to provide corrosion protection is most often enhanced by the introduction of various anti-corrosion additives. The most commonly used is zinc and its compounds [7], for example in ZincRich powder coatings manufactured by TIGER Drylac [8]. The anticorrosive effect of zinc-doped coatings is mainly cathodic protection. Zinc oxidises and protects the steel substrate from oxidation. As the zinc oxidises, the coating loses its conductive properties and the galvanic protection becomes weaker. The coating then still provides corrosion protection to the substrate, but only on a barrier and inhibition basis by the corrosion products of the zinc [9]. However, despite their popularity, zinc compounds pose a threat to the environment due to their toxicity. The classification of zinc as a hazardous substance has contributed to the search for new solutions [10]. In many of these, zinc has been replaced by phosphate pigments, mainly zinc phosphate [11]. This applies to most of the so-called zinc-free products on the market. However, recent studies have shown the harmful effects of phosphates on aquatic organisms, so their use should be progressively restricted under Directive 2000/60/EC [12].

In addition, zinc phosphate has a weaker anticorrosive effect than zinc, therefore in order to achieve adequate corrosion protection, it is recommended to apply thicker coatings, which in turn is associated with higher paint consumption and deterioration of other coating parameters with increasing thickness, such as adhesion to the substrate, impact strength, flexibility, ductility, to which powder coatings are particularly sensitive. Adhesion to the substrate can be increased by perfect surface preparation, but in some cases this is difficult to achieve, for example in polluted air or when the geometry of the object to be protected is complex.

These facts make it necessary to develop new coatings with environmentally friendly additives, e.g. in the form of allotropic carbon variants [13–15]. The popularity of graphene, associated with its remarkable electrical properties and superior mechanical strength, has encouraged its use in the coatings industry. Many researchers have shown that the addition of graphene to coatings increases their mechanical strength and enhances the corrosion protection of coated materials. One example is a polyester coating containing 2% graphene demonstrating higher thermal stability and mechanical strength compared to an unmodified sample [16]. An increase in thermal conductivity, fracture toughness and impact strength was also observed for the graphene-modified epoxy coating [17]. An increase of 522% in Young's modulus and 242% in hardness was also observed for an acrylic coating containing 2% graphene [18], while a 0.5% addition of graphene to a polyurethane coating contributed to a 2-fold increase in Young's modulus [19]. In addition, pure graphene coatings isolate corrosive media from the substrate and provide effective metal protection [20].

However, the production of graphene-based paints and coatings is hampered by its poor dispersion in organic solvents or water and its poor compatibility with many resins. In addition, the extraction of graphene is rather cumbersome, time-consuming and expensive [21]. For this reason, graphene oxide (GO) is more commonly used as a modifier. The structure of graphene oxide is formed by unsaturated six-membered rings and oxidised cycloaliphatic rings. An important difference between graphene and its oxidised form is the sp3 hybridisation of the oxidised carbon atoms [22]. Due to its more polar structure, it is easily dispersed in water and other polar solvents as the graphene oxide molecules take on a negative charge and stabilise the dispersion through electrostatic interactions [23]. Graphene oxide also has a much higher reactivity than the non-oxidised form of graphene, which is particularly important in the manufacture of polymer composites due to its greater compatibility with resins [16].

The modification of epoxy-polyester powder coatings with graphene oxide has been described in the work of Li et al. [24]. A cross-linked coating containing 1.5 wt% GO, after immersion in a 3.5 wt% NaCl solution for 9 days, showed a 74.1% reduction in corrosion current and a 34.2% increase in corrosion potential compared to the unmodified sample. An increase in the abrasion resistance of the coatings was also observed, but only when the GO was well dispersed [25].

In addition to anti-corrosive additives, the choice of resin has a significant impact on the protective properties of the powder coating. The vast majority of powder coatings produced today are based on thermosetting resins, which include epoxy, epoxy-polyester, silicone and even acrylic resins. When heated, the thermoset resin melts and liquefies, followed by a cross-linking reaction, resulting in a cross-linked coating. The curing of this type of product is irreversible and the resulting coating is non-fusible and insoluble. The temperature at which the resin melts and cross-links to form a homogeneous polymeric coating is usually lower than for thermoplastic polymers and is in

the range of 160–230°C [26]. Nevertheless, the curing process for conventional thermoset coatings is energy intensive. In order to reduce the energy intensity of this process, research is underway to develop coatings that cure at lower temperatures. The first crosslinkers and low temperature resins have appeared on the market, including products such as VESTANAT B 1358/100 (Evonic) and Uralac Ultra (Covestro). Hydrophobic blocked polyisocyanates (PICs) that allow the coating to cure below 160°C have been described in papers [27].

An important factor in achieving effective corrosion protection is very good adhesion to the substrate. Of the resins available on the market, epoxy resins demonstrate the best adhesion, but are used as primers or indoors due to their poor light resistance.

Functionalised polyester or acrylic resins are used to lend powder coatings very good mechanical strength, UV resistance, chemical passivity and also high aesthetic qualities [28]. The protective properties of coatings are improved by various types of modification, e.g. with chemically incorporated polysiloxanes [29].

The aim of the present study was to investigate the effect of graphene oxide on the physical, mechanical and protective properties of low-temperature powder coatings based on acrylic resins. An *in situ* method was used to facilitate the dispersion of GO in the paint. The properties of the modified coatings were evaluated by measuring roughness, gloss, adhesion to the substrate, hardness, scratch resistance, contact angle and ductility. The effect of graphene oxide on the protective properties of the coatings was investigated using electrochemical impedance spectroscopy (EIS).

2. Characteristics of the raw materials used and the test methodology

2.1. Raw materials

The raw materials used to synthesise the acrylic resin included 2-hydroxyethyl methacrylate (HEMA) (Merck, Germany), methyl methacrylate (MMA, Sigma Aldrich, Germany), *n*-butyl acrylate (BA, Sigma Aldrich, Germany), graphene oxide (supplied by the Łukasiewicz Research Network-Institute of Microelectronics and Photonics in Warsaw, commercially known as G-Flake GO; the method for obtaining G-Flake GO and its characterisation is described in the paper [30]), and azabisisobutyronitrile (AIBN, Sigma Aldrich, Germany).

The raw materials used to obtain the powder paint included VESTANAT B 1358/100 (Evonik Industries, Germany), spreading agent Resiflow PV 88 (Worlee Chemie GmbH, Germany), benzoin as a degassing agent (Sigma Aldrich, Switzerland).

2.2. Methodology for the synthesis of acrylic resins and their modification

The acrylic resin was prepared according to the methodology described in an earlier paper [31], using the three monomers 2-hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA), and *n*-butyl acrylate (BA) in a molar ratio of 1 : 5 : 2, respectively [24]. Graphene oxide was dispersed in the monomer mixture, followed by the addition of AIBN to initiate the polymerisation reaction. The unmodified resin was designated HEMA/5MMA/2BA, whose individual members are derived from the abbreviation of the name and molar ratio of the monomers used in its synthesis. On the other hand, acrylic resins con-

taining 0.5 wt%, 1 wt% or 3 wt% graphene oxide are designated with symbols containing at the end the percentage of graphene oxide (GO) relative to the total weight of the resin, e.g. HEMA/5MMA/2BA/0.5GO.

2.3. Obtaining powder paint and coatings

The following were used to obtain the powder paints: synthesised unmodified acrylic resin (LOH = 40 mg KOH/g) HEMA/5MMA/2BA and modified resins containing 0.5 wt%, 1 wt% or 3 wt% graphene oxide (GO), respectively. Commercial VESTANAT B 1358/100 was used as a crosslinking agent, the amount of which was calculated on the basis of the LOH value of the acrylic resin so that the molar ratio of −NCO groups to −OH groups was 1 : 1. In addition, Resiflow PV 88, a spreading agent, and benzoin as a degassing agent were used. The aforementioned raw materials were mixed and the resulting paint compositions were milled and then extruded using an EHP 2 × 12 Sline co-rotating twin-screw extruder manufactured by Zamak (Poland). The temperature of the individual zones in the extruder was as follows: zone I: 85°C, zone II: 95°C, zone III: 100°C, link: 105°C. The screw speed was 150 rpm. After extrusion, the paints were cooled, ground and sieved through a 100 μm mesh sieve. The surface of the metal plates was cleaned, degreased and subjected to zirconium phosphate conversion in 1.5% ESKAPHOR Z 2000 C solution. The produced powder coatings were applied to the dried steel plates using the corona electrostatic method with a PEM-X1 Wagner gun (Alstatten, Switzerland). The sputtering parameters were as follows: electrode voltage 60 kV, current 30 μA. The coatings were cured at 160°C for 15 min. The powder coatings produced are designated with symbols starting with the letter "L", while their successive members are derived from the type of resin used: unmodified acrylic (L_HEMA/5MMA/2BA) and graphene oxide-modified GO (e.g. L_HEMA/5MMA/2BA/0.5GO). A schematic showing the powder coating sample production line is provided in Fig. 1.

2.4. Characteristics of the paints and coatings obtained

2.4.1. Differential scanning calorimetry (DSC)

The curing process and thermal properties of the resin were investigated using differential scanning calorimetry (DSC). The measurement was carried out using a Mettler Toledo 822e calorimeter equipped with StareSystem software. The analysis resulted in a thermogram showing the relationship between heat flux and temperature. Calibration of the DSC apparatus was carried out using indium and tin standards provided by Mettler Toledo. The mass of the samples analysed was approximately 10 mg. The samples were weighed to the nearest 0.00001 g, after which they were hermetically sealed in standard 40 μl aluminium crucibles and placed in a measuring chamber. The reference sample consisted of an empty aluminium crucible. Analyses were performed under a nitrogen atmosphere with a gas flow rate of 60 ml/min and a heating rate of 20 K/min between 0°C and 200°C.

2.4.2. Polymerisation test

The polymerisation test consisted of lightly rubbing the coatings with a swab soaked in methyl ethyl ketone (MEK) back and forth 30 times in each direction to check that the coating was fully cured. The coatings were assessed using the guidelines contained in the technical requirements of the QUALICOAT quality mark [32]. After
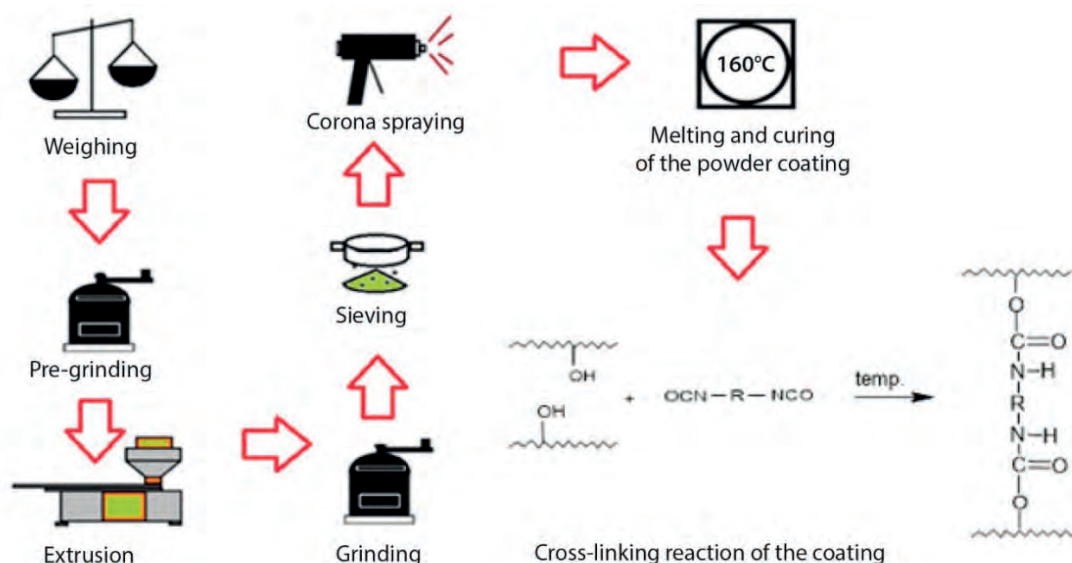
Fig. 1. Powder paint production flow chart

Rys. 1. Schemat wytwarzania powłok proszkowych

30 min of rubbing, the samples were evaluated and classified according to the following criteria: the coating is matt and soft (1), the coating is matt and can be scratched with a fingernail (2), slight loss of gloss (3), no noticeable change (4). The polymerisation test was carried out twice for each coating.

2.4.3. Flowability

In accordance with EN ISO 8130-11, the evaluation of paint flow from an inclined surface was carried out. Cavities with a depth of 6.5 mm and a diameter of 25 mm were stamped into the steel test plates. Then, a paint sample of 0.5 g was placed in the cavity of the plate and positioned at 60° from horizontal in an oven heated to 160°C for 15 min. After this time, the distance between the bottom edge of the cavity and the furthest point where the melted powder paint flowed was determined.

2.4.4. Roughness

The test was carried out using the profile method with a Mahr GmbH Göttingen, Mar SurfPS1 gauge in accordance with EN ISO 12085. Measurements were made at 21°C ±0.1°C, LT = 5600 mm and LC = 0.800 × 5 N. Using a head sliding over the surface of the coating, the two basic roughness parameters Ra (arithmetic mean deviation from the baseline expressed in μm) and Rz (arithmetic mean of the 5 highest profile elevations minus the arithmetic mean of the 5 lowest profile depressions expressed in μm) were measured. Measurements were taken at ten different locations on the surface of the same coating. The final result was the arithmetic mean of these measurements.

2.4.5. Gloss

Gloss was measured using a BYK-Gardner micro-Tri-gloss-μ glossmeter according to the guidelines of EN ISO 2813. Measurements were taken of the intensity of light reflected from the coating when viewed at an angle of 60°. Ten measurements were made for each sample. The arithmetic mean of the results obtained was taken as the final result.

2.4.6. Adhesion to steel substrate

The test of adhesion to the steel substrate was carried out using a special knife with 6 circular blades, spaced 2 mm apart, using the notch grid method according to EN ISO 2409. The notches were made perpendicular to each other so that they formed a grid of squares. The surface was cleaned with a brush, then a 50 mm wide adhesive tape with standardised peel strength was applied. After 5 min, the tape was peeled off and the appearance of the grid was assessed. The coatings were graded on a scale of 0 to 5, where 0 meant no marks other than blade marks, while 5 meant nearly complete or complete detachment of the coating. The test was repeated twice for each type of coating.

2.4.7. Hardness

The hardness of the coatings was tested according to EN ISO 1522 using a BYK-Gardner König pendulum. During the measurement, the ratio of the decay time of oscillation of a pendulum placed on the test specimen to the glass constant was measured. The glass constant was 171 s. Three measurements were made for each series of coatings. The arithmetic mean of the results obtained was taken as the final result.

2.4.8. Scratch resistance

The scratch resistance of the coating was measured by placing a coated panel on the instrument table and then sliding a stylus with a 1 mm diameter semicircular tip across the panel. The load was increased by 50 g until a scratch was visible on the coating. This was done using an Elcometer Clemens manual tester in accordance with EN ISO 1518. Measurements were taken on three samples of each type. If the result for the three samples did not differ, its was taken as the final result.

2.4.9. Contact angle

The contact angle is the angle formed between the surface of the coating being tested and the tangent to the surface of the measured droplet deposited on the coating at the interface between the

three phases: solid, liquid and gas. The contact angle was determined using an OCA 15 optical goniometer equipped with a Data Physics automatic droplet dispenser module in accordance with PN-EN 828. The contact angle was measured by placing the sample on the measuring table of the goniometer and then applying a 1 µl drop of the measuring liquid (water) to the surface. The shape of the droplet was recorded by a camera and the droplet contours and contact angle were determined using SCA20U computer software. Ten measurements were made for each coating tested. The arithmetic mean of these measurements was taken as the final result.

2.4.10. Ductility

The cupping test was performed in accordance with EN ISO 1520 using TQC's SP4300 manual tester. The measurement consisted of pressing a spherical piston into an immobilised sample until the coating cracked. The measurement was performed on three samples of the same type.

2.4.11. Electrochemical impedance spectroscopy (EIS)

In order to assess the resistance of the coatings to corrosive conditions, an electrochemical impedance spectroscopy (EIS) test was performed. The measurement was carried out in a solution of 3.5 wt% NaCl, at room temperature for 7 days. The working electrode (WE) consisted of an isolated section of the sample surface with a diameter of 35 mm (area 9.62 cm^2), the reference electrode (RE) was a saturated chlorosilver electrode (Ag|AgCl|KCl(sat.), +0.197 V relative to the normal hydrogen electrode (NHE) and the counter electrode (CE) consisted of a platinum grid with an area of 20 cm^2. A voltage excitation signal with an amplitude of 10 mV (rms) and a frequency ranging from 100 kHz to 100 mHz was applied. The fitting of the equivalent circuit to the obtained measurement data was performed in ZSimpWin 3.21 (Echem Software, USA).

3. Selection of monomers for the acrylic resin

Powder coatings based on acrylic resins are characterised by excellent weather resistance, colour durability, good physical and mechanical properties such as high scratch resistance, hardness or adhesion to the substrate [33]. The disadvantage of acrylic coatings is their low flexibility. Acrylic resins used for powder coatings usually have hydroxyl, carboxyl or epoxy functional groups (Table 1) [34]. Resins containing hydroxyl groups in their structure show the best flexibility. Blocked polyisocyanates are usually used as crosslinkers for this type of resin. Urethane bonds are formed during the reaction between the −NCO groups formed after unblocking the crosslinker and the −OH groups derived from the acrylic resin. Polyurethane-acrylic coatings crosslinked in this way are characterised by high weather resistance, provided the polyisocyanate is based on an aliphatic or cycloaliphatic diisocyanate. The coating obtained by crosslinking an acrylic resin containing carboxyl groups is characterised by very good adhesion to the substrate and resistance to atmospheric agents. On the other hand, crosslinking an acrylic resin containing epoxy groups produces a coating with excellent adhesion to the substrate but poor UV resistance. Powder coatings based on epoxy resins are increasingly used in the furniture industry because they can be cured on heat-sensitive substrates such as wood, plastics and medium density fibreboard (MDF) [35]. This is due to their ability to crosslink by a rad-

Table 1. Classification of acrylic resins based on the presence of functional groups
Tabela 1. Podział żywic akrylowych ze względu na obecność grup funkcyjnych

Type of functional groups contained in the acrylic resin	Hydroxyl −OH	Carboxylic −COOH	Epoxy
Cross-linking agent	blocked polyisocyanates (PIC)	epoxy resins	carboxylic acids
Advantages of the coatings	very good weather resistance	very good adhesion to the substrate, high hardness	very good adhesion to substrate, corrosion protection
Disadvantages of the coatings	poor impact strength	low flexibility	no resistance to UV radiation

Source: [28, p. 285; 34, p.179].

Źródło: [28, s. 285; 34, s, 179].

ical or ionic photopolymerisation mechanism in the presence of photoinitiators and UV radiation [36].

A very important aspect in designing the chemical composition of acrylic resins is the selection of the appropriate monomers. The source of hydroxyl groups in this study was 2-hydroxyethyl methacrylate (HEMA). Methyl methacrylate (MMA) and *n*-butyl acrylate (BA) were also used in addition to HEMA [37]. MMA was used the most extensively compared to the other monomers (the molar ratio of HEMA : MMA : BA was 1 : 5 : 2). This was because MMA, due to the presence of a stiffening −CH3 methyl group on the double bond in the *α*-position, had the task of imparting sufficient stiffness to the HEMA/5MMA/2BA resin (*Tg* = 40.4°C) [38]. Too little MMA could have resulted in clumping of the powder coating during storage and deposition on the gun walls during spraying. BA was used to provide sufficient flexibility due to the presence of an aliphatic chain at the substituent in the ester group which acts as a plasticiser [32]. Azobisisobutylonitrile, 2-(2-cyanopropan-2-yl-diazenyl)-2-methylpropanonitrile (AIBN), was used as a radical polymerisation initiator. Unlike organic peroxides, this initiator does not form oxidised by-products and does not cause oxidative degradation of the pigmented resins.

4. Research results and discussion

4.1. Purpose of the article

The main task of any coating, apart from providing protection for the coated materials, is to be aesthetically pleasing and durable. In order to assess whether the coatings tested fulfilled these tasks, they were subjected to gloss, roughness, hardness, ductility, scratch resistance, adhesion to the substrate and contact angle tests. To obtain the coatings, the paints were sprayed onto test panels and cured at 160°C for 15 min. The cross-linking process of the coatings was investigated using DSC, while the corrosion protection ability was investigated using EIS spectroscopy.

4.2. Paint modification with graphene oxide

Dispersing GO in powder coatings is a very difficult task. Adding graphene oxide directly to the powder coating formulation at the raw material weighing stage, followed by homogenisation in
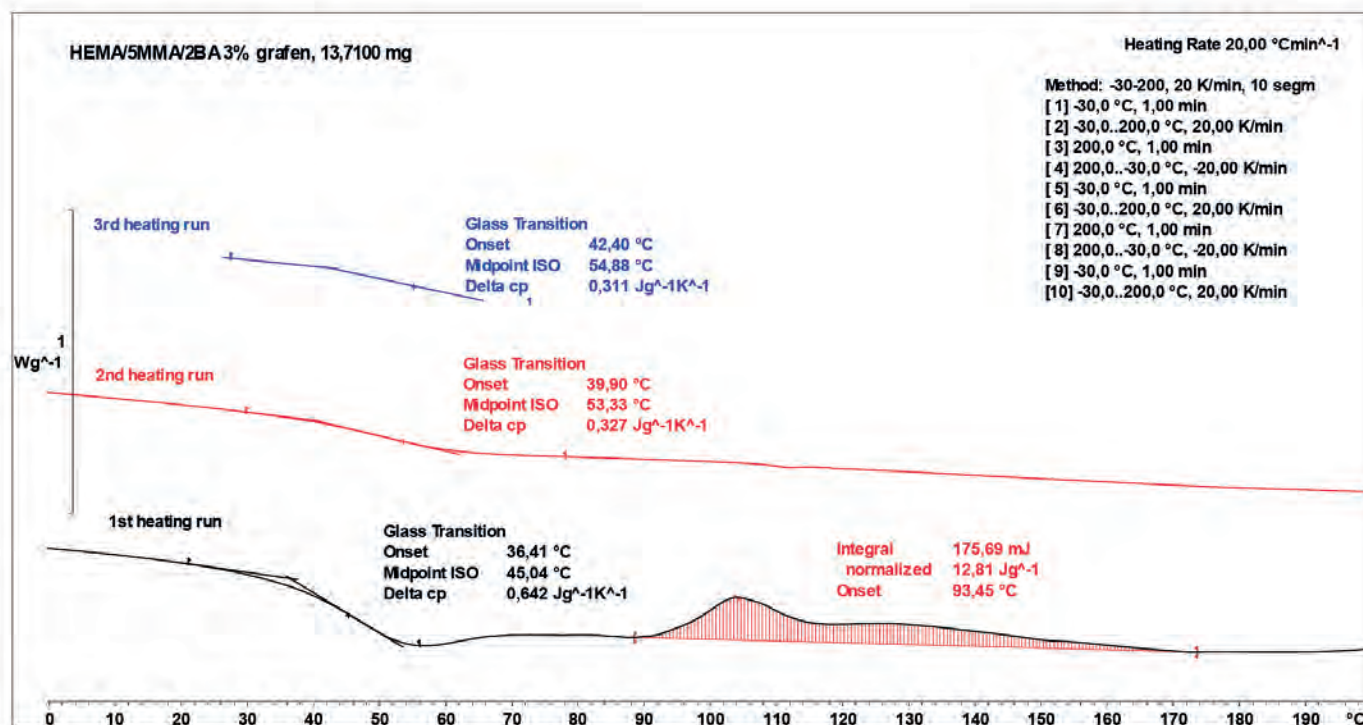
Fig. 2. DSC thermogram of sample L_HEMA/5MMA/2BA/3GO

Rys. 2. Termogram DSC próbki L_HEMA/5MMA/2BA/3GO

the molten state, does not result in adequate dispersion. Graphene oxide (GO) agglomerates were visible in the cross-linked coatings. Better dispersion was achieved by mixing graphene oxide with acrylic monomers followed by an *in situ* polymerisation reaction.

4.3. Cross-linking reaction time of powder coating

After mixing the modified resin with a cross-linking agent and an additive to improve flow and facilitate degassing, powder paints were prepared by homogenisation in an extruder, then ground and sieved on a 100 µm mesh sieve.

Differential scanning calorimetry (DSC) analyses were carried out on 3 sample heating and cooling cycles to investigate the cross-linking reaction of the coatings (Fig. 2). During the first heating cycle of the coating, in the 30–60°C range, the transition of the resin, which is the main component of the paint, from the glassy to the elastic state is visible. In the 90–160°C range, an exothermic peak is observed during the same heating cycle, indicating the course of the paint's cross-linking reaction. The temperature range recorded (90–160°C) is lower than that of classical thermosetting paints (140–200°C), allowing the tested paints to be classified as low-temperature. The thermograms obtained during two successive heating cycles confirm the complete cross-linking of the sample during the first cycle due to the absence of exothermic peaks in the 90–160°C range. Furthermore, the cross-linking of the paints is confirmed by the slight difference in the glass transition temperature ($\Delta Tg = +1.55°C$) between the 2nd and 3rd heating cycles, which should not be greater than −2°C and +3°C, respectively.

In addition, the cross-linking of the coatings was confirmed by a polymerisation test. After 15 min in an oven heated to 160°C and cooling to room temperature, they were rubbed back and forth 30 times with a swab soaked in methyl ethyl ketone (MEK). After 30 min, no changes such as matting or softening were observed on the surface of the coatings. This confirmed that each of the coatings produced exhibited a high degree of cross-linking, indicating the selection of an appropriate 1 : 1 molar ratio of −NCO groups of the cross-linking agent to −OH of the resin equal to 1 : 1, as well as the correct curing conditions.

4.4. Characteristics of physical and mechanical properties

Once the powder coatings had cured, their physical and mechanical properties were investigated. Table 2 summarises the results obtained.

The coatings obtained were characterised by the absence of defects in the form of craters or orange peel, although one of the coatings (L_HEMA/5MMA/2BA/3GO) containing 3% GO was clearly distinguished by its greater roughness, which was a consequence of its lack of tendency to flow. The flowability of the other coatings also decreased with increasing GO content. The increase in roughness also contributed to a decrease in gloss of this coating. The remaining samples were characterised by low roughness ($Ra < 1$ µm). All the coatings tested exhibited the highest degree of adhesion to the steel substrate $Gt = 0$. No voids were observed along the cuts on any of the coatings obtained. When investigating the effect of graphene oxide on relative hardness, it was found that an increase in the hardness of the coatings occurred for samples containing 0.5 wt% and 1 wt% GO. With further increases in GO up to 3 wt%, a decrease in hardness is observed due to a deterioration in the compatibility between GO and the coating components. Too high a hardness of coatings is not recommended as very hard coatings are not resistant to elastic deformation. The scratch resistance of coatings is closely related to the chemical structure. The coating without the modifier L_HEMA/5MMA/2BA showed a very high scratch resistance and the addition of GO did not significantly enhance this property. The presence of graphene oxide also

Table 2. Summary of physical and mechanical parameters of the produced coatings
Tabela 2. Zestawienie parametrów fizyko-mechanicznych wytworzonych powłok

| Physical and mechanical parameter	Coating symbol			
	L_HEMA/5MMA/2BA	L_HEMA/5MMA/2BA/0,5GO	L_HEMA/5MMA/2BA/1GO	L_HEMA/5MMA/2BA/3GO
Flow [mm]	24	18	0	0
Roughness: Ra Rz	0.40 ±0.02 2.02 ±0.12	0.39 ±0.03 1.65 ±0.18	0.44 ±0.02 2.07 ±0.21	1.10 ±0.06 4.56 ±0.17
Gloss 60°C [GU]	74.10 ±1.10	57.30 ±1.51	54.03 ±1.85	39.43 ±0.55
Adhesion to the steel substrate [0 – good 5 – bad]	0	0	0	0
Relative hardness [–]	0.61 ±0.03	0.71 ±0.05	0.71 ±0.02	0.60 ±0.05
Scratch resistance [g]	700	650	700	800
Contact angle [deg]	85.30 ±1.2	91.03 ±2.94	91.07 ±3.31	82.43 ±3.23
Ductility [mm]	3.20 ±0.2	7.60 ±0.2	4.00 ±0.4	2.70 ±0.3
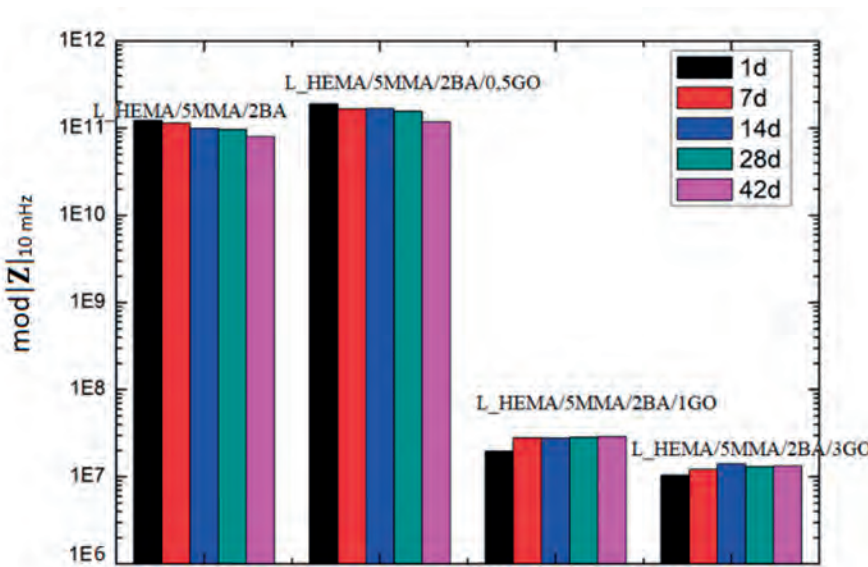
Fig. 3. Values of mod$|\mathbf{Z}|_{10\,mHz}$ for the tested coatings performed 42 days after immersion of the coatings in a 3.5 wt% NaCl solution

Rys. 3. Wartości mod$|\mathbf{Z}|_{10\,mHz}$ uzyskane po 42 dniach od zanurzenia powłok w roztworze NaCl 3,5% wag.

contributed to an increase of the coatings' hydrophobicity. However, at 3 wt% GO content, the roughness of the coating increased, which may be the reason for the lower water contact angle value.

A ductility test was carried out to assess the resistance of the applied coatings to cracking, e.g. during the formation of painted sheet metal. Coatings with poor ductility cannot be applied to materials from which complex shaped parts are formed. The observed increase in the ductility of coatings containing GO is due to the high flexibility of this modifier. The introduction of graphene oxide into acrylic resin by the *in situ* method solves the problem of acrylic resins' low elasticity. The presence of GO at 0.5 wt% contributed to an increase of more than 100% in the ductility of L_HEMA/5MMA/2BA. A further increase in the GO content resulted in a decrease in ductility, which may be related to the deterioration of the GO dispersion due to insufficient interaction of the polar functional groups of the resin with GO, which are too few to penetrate into all the GO interlayer spaces, resulting in an increase in distances that separate them.

4.5. Characteristics of the corrosion resistance of coatings

In addition to the physical and mechanical properties, the protective performance of the coatings in a highly corrosive environment was evaluated. Electrochemical impedance spectroscopy (EIS) tests were carried out to assess the corrosion performance of the coatings. The results of the EIS measurements were visualised using Bode plots (Fig. 3); Fig. 4 also shows the changes in the mod$|\mathbf{Z}|_{10\,mHz}$ values recorded over the 42 days of measurements.

The corrosion resistance of the coatings was assessed using the impedance modulus, which varies with frequency. The higher the value of the impedance modulus, the higher the corrosion resistance of the coating.

The values of the impedance modulus were recorded at low frequencies, as they are indicative of better corrosion properties. By analysing the graph shown in Fig. 3, it can be seen that the L_HEMA/5MMA/2BA and L_HEMA/5MMA/2BA/0.5GO coatings show 4 orders of magnitude higher impedance values compared to the
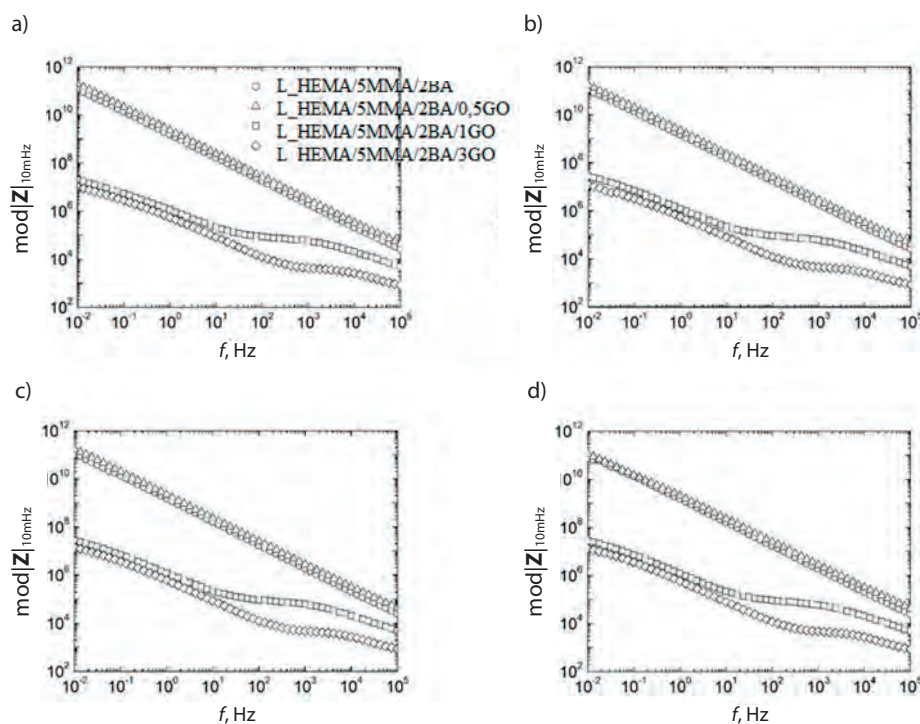
a)

b)

c)

d)

Fig. 4. Bode plots showing the relationship between the impedance modulus and frequency, taken after: a) 1 day, b) 7 days, c) 14 days, d) 42 days after immersion in 3.5 wt% NaCl solution

Rys. 4. Wykresy Bodego przedstawiające zależność modułu impedancji od częstotliwości, wykonane po: a) 1 dniu, b) 7 dniach, c) 14 dniach, d) 42 dniach od zanurzenia w roztworze NaCl 3,5% wag.

L_HEMA/5MMA/2BA/1GO and L_HEMA/5MMA/2BA/3GO coatings. The introduction of a small amount of graphene oxide (0.5 wt%) does not change the capacitive nature of the coating (one time constant), as can be seen in Fig. 4. However, an increase in impedance values is observed compared to the undoped GO coating. For L_HEMA/5MMA/2BA and L_HEMA/5MMA/2BA/0.5GO, the $mod|Z|_{10\,mHz}$ values in the corrosive environment decreased from 123 to 80 [G$\Omega \cdot$ cm^3] and from 190 to 118 [G$\Omega \cdot$ cm^2], respectively, over the duration of the experiment.

In the Bode spectra of the L_HEMA/5MMA/2BA/1GO and L_HEMA/5MMA/2BA/3GO coatings, two capacitive loops can be observed at high (100 kHz–100 Hz) and low (100 kHz–10 mHz) frequencies, indicating the presence of two time constants. The low frequency loops characterise the properties of the coatings, while the high frequency loops characterise the corrosion processes taking place.

The coating L_HEMA/5MMA/2BA/3GO shows the lowest corrosion resistance. In addition, for this coating and for L_HEMA/5MMA/2BA/1GO, a slight increase in the modulus values was observed during the experiment from 20 to 29 [M$\Omega \cdot$ cm^2] and from 10 to 13 [M$\Omega \cdot$ cm^2] respectively, indicating a partial sealing of these coatings during conditioning in the corrosion medium by the corrosion products formed.

The L_HEMA/5MMA/2BA/0.5GO coating showed the highest corrosion inhibition capacity, therefore defining the optimum graphene oxide content in the coating at 0.5 wt%. Its higher amount has a negative effect on the ability to protect the steel substrate against corrosion. It should be noted that the anticorrosion properties of coatings are closely related to their mechanical properties. Coatings with poorer mechanical properties are more easily damaged, allowing corrosive media to reach the substrate more quickly.

5. Conclusion

In this study, low temperature powder coatings based on graphene oxide modified acrylic resins were obtained. The resulting acrylic resins, which constitute copolymers of HEMA, MA and BA in a molar ratio of 1 : 5 : 2, show high hardness and scratch resistance. The introduction of graphene oxide by the *in situ* method at the resin synthesis stage has a favourable effect on the properties of the coatings formed, unlike when it is dosed into the paint at the raw material weighing stage. The *in situ* method allowed good dispersion of the graphene oxide in the resin and increased compatibility with the other coating components.

The cross-linking process of the coatings studied using the DSC technique allows the tested coatings to be classified as low-temperature, which is extremely important when curing coatings on substrates with low thermal resistance, such as plastics or MDF boards. This method, in combination with the polymerisation test, makes it possible to assess whether the coating is fully cross-linked under certain conditions.

Based on the tests conducted, it was found that with increasing GO content in the paint, an increase in roughness, a decrease in gloss of the coatings and a decrease in water repellence were observed. The coating with the highest graphene oxide content (3 wt%) showed the lowest ductility, hydrophobicity, hardness and corrosion resistance. The L_HEMA/5MMA/2BA/0.5GO coating had the best toughness properties. The presence of 0.5 wt% graphene oxide had a positive effect on the ductility of the coatings, which

increased by a factor of 2 compared to the reference sample. The cross-linked L_HEMA/5MMA/2BA/0.5GO coating is hydrophobic, anticorrosive and has very good strength properties, demonstrating that 0.5% GO constitutes a very good modifier for acrylic resins intended for powder paint.

CRediT authorship contribution statement

Katarzyna Pojnar: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

Barbara Pilch-Pitera: Data curation, Funding acquisition, Project administration, Resources, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

Natalia Roś: Investigation, Validation.

Łukasz Florczak: Formal analysis, Software, Validation, Visualization.

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ul. Czackiego 3/5, 00-043 Warszawa
Telefon: +48 22 250 22 10; Kom: +48 785 870 461; e-mail: sekretariat@not.org.pl