Novel Concepts of Acrylic Resin Application in Powder Coatings Formulation

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Introduction

Due to the various forms in which film-forming substances occur, we can divide them into those containing organic solvents, including high-solids, water-dilutable, and powder coatings. The key features of any coating material are to provide aesthetic or decorative value, protective qualities, and to achieve specific functional properties [1]. Coatings should possess good physico-mechanical properties such as durability, excellent adhesion, and resistance to weather conditions, as well as chemical and thermal resistance. The standard solvent based coatings characterized by high performance properties but containing organic solvents such as toluene, hexane, and methanol. During World War II, their production increased significantly. This fact contributed not only to the development of the industry but also to ecological problems. The consequence of these actions is the increasingly noticeable change in our climate through global warming and various types of catastrophes in the world. [2].

Powder coatings, which were first produced in the 1940s, were based on thermoplastic resins. In the 1950s, powder coatings based on epoxy resin were developed at the Shell laboratory in Delft. Since then, depending on customer requirements and applicable standards, the market for paints and varnishes has become one of the most dynamic sectors of the chemical industry. The development of new coating compositions that comply with current standards, directives, and consumer requirements has led to the creation of various coating products. Additionally, powder coatings meet the so-called "5E" criteria. [3]:

- Efficiency - powder coatings are most commonly applied using the Corona electrostatic method. This method allows reused application of powder to a given part, which can consequently lead to increased productivity and reduced production costs.
- Economy - although the initial investment in equipment for producing powder coatings may be higher compared to liquid systems, powder coatings prove to be more cost-effective in the long run. The ability to recycle the powder that remains in the chamber after application, or to re-spray in case of an incorrect application by blowing it off the uncured part, reduces material waste and lowers energy consumption, thus reducing costs.

- Energy Savings – due to the absence of solvents, powder coatings do not require drying time as is necessary with commonly used liquid systems, thereby shortening production time. Additionally, ongoing research on curing coatings at low temperatures or UV curing allows for reduced energy consumption.
- Environmental Compliance - one of the greatest advantages of powder coatings is their environmental friendliness. Unlike liquid coatings containing VOCs, powder coatings are free of solvents. They increasingly contribute to a more sustainable industry ecologically, reducing air pollution and minimizing health risks for both humans and the environment.
- Excellence of Finish - powder coatings exhibit good performance properties. Compared to liquid systems, they are characterized by better adhesion and anti-corrosion properties. Once cured, they form a durable and resistant layer that can withstand harsh environmental conditions, including exposure to UV radiation, moisture, chemicals, and extreme temperatures.

This work focuses on addressing issues related to powder coatings, such as lowering curing temperatures and thereby reducing production costs, developing new powder coating formulations that do not contain VOCs, and ensuring they have the appropriate performance properties that determine the final application of the powder coating. To better interpret the results, powder coating based of acrylic resins were categorized based on the presence of functional groups, including hydroxyl and epoxy groups. Low-temperature systems and UV-curing methods enabled the application of coatings on temperature-sensitive materials, such as magnesium alloys, MDF boards, and wood. Developing an appropriate acrylic resin formulation for powder coatings solved the problem of low flexibility and allowed for the production of powder coatings with good physico-mechanical properties. Additionally, based on the tested acrylic resins and appropriate additives, powder coatings with specific properties such as anti-corrosive, antibacterial, and high hydrophobic parameters were developed. Antibacterial coatings containing natural biocides, without silver, further enhance the ecological aspect.

Method

The acrylic resins used to the powder coating were obtained through free-radical bulk polymerization. This method was chosen for ecological reasons (solvent-free) and to achieve a high average molecular weight, which is a favorable parameter considering the requirements for powder coating production. The obtained acrylic resins, powder coatings and finished powder coatings were characterized using a range of research techniques. The chemical structure of the acrylic resins was confirmed using Nuclear Magnetic Resonance (NMR) spectroscopy and Fourier Transform Infrared (FT-IR) spectroscopy. To check the average molecular weight (M_n) and the degree of polydispersity (M_w/M_n), Gel Permeation Chromatography (GPC) was used. The glass transition temperature (T_g) and viscosity of the acrylic resins were determined to assess whether the resin is suitable for the next stage of paint formulation and for storing powder coatings under standard ambient conditions. Thermal analysis of the resin, powder coating, and curing process was characterized using Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA) and Thermogravimetric Analysis (TGA/DTG). The properties of the obtained powder coatings were evaluated according to the current standards and technical requirements of the QUALICOAT quality mark for paints, varnishes and powder coatings. Additionally, surface analysis was conducted using an optical microscope with polarization and with or without elemental analysis. Microstructures, morphologies, and compositions of the obtained coatings were analyzed using Scanning Electron Microscopy (SEM) combined with Energy Dispersive Spectroscopy (EDS). Efforts were also made to explain the mechanism of action of antibacterial additives using the Kelvin Probe Scanning Method (SKP). All the techniques used were described in detail in the articles on which this work is based.

Results and discussion

Thanks to the wide range of available acrylic monomers on the chemical market, a series of acrylic resins for powder coatings was designed, which influenced the final properties and applications of the powder coatings.

Studies on the Synthesis of Acrylic Resins Containing Hydroxyl Functional Groups for Powder Coatings

The main monomer containing a hydroxyl group used was 2-hydroxyethyl methacrylate (HEMA). The use of HEMA, along with a crosslinking agent at the appropriate temperature, facilitated the crosslinking process between the hydroxyl group and the isocyanate group in a 1:1 stoichiometric ratio. Another very important monomer was methyl methacrylate (MMA). The presence of the methyl group at the α-bond enabled the creation of a thermally stable coating composition. However, an excessive amount of MMA in the coating led to high hardness and brittleness. For this reason, butyl acrylate (BA) was used. The four-carbon hydrocarbon chain allowed for increased flexibility of the coating. The monomers 2-hydroxyethyl methacrylate, methyl methacrylate, and butyl acrylate formed the basis for the synthesis of the acrylic resin.

Based on the HEMA:5MMA:2BA resin, the publication titled "Polyacrylate Resins Containing Fluoroalkyl Groups for Powder Clear Coatings" investigated the impact of fluorinated monomers on the final properties of the coating [4]. Fluorinated derivatives used included acrylic and methacrylic monomers of 2,2,2-trifluoroethyl. The fluoroalkyl groups influenced the performance properties of the powder coatings. These coatings exhibited good gloss, hardness, scratch resistance and adhesion to the substrate. The resulting powder coatings, with increased hydrophobicity, can be used outdoors to protect material surfaces from environmental factors such as moisture and mechanical stresses. Additionally, the impact of 2-phenoxyethyl acrylate (PhEA) was examined, which enhanced the gloss and flexibility of the coating.

Continuing the work on acrylic resins containing hydroxyl groups, subsequent research led to the development of a study on powder coatings characterized by protective properties and the capability to cure at low temperatures (referred to as low-temperature systems) [5]. To obtain low-temperature powder coatings, blocked isocyanates synthesized under laboratory conditions using methyl ethyl ketoxime (MEKO) were employed, allowing the curing temperature to be reduced to 160°C for 20 minutes. Additionally, the properties of powder coatings based on acrylic resin were compared with those of a commercial polyester resin, SIRALES. The obtained powder coatings were evaluated for properties such as roughness, gloss, adhesion to steel substrates, hardness, scratch resistance, hydrophobicity and resistance to liquids. Furthermore, in addition to the immersion test in a NaCl solution, electrochemical impedance spectroscopy (EIS) in a 3.5% NaCl solution was used to provide a more comprehensive assessment of the corrosion protection capability of the coatings. The powder coatings based on acrylic resin demonstrated better resistance to water, mechanical damage, and corrosive media compared to those made with the commercial polyester resin. The additional silicon content in the blocking agent increased the contact angle of the powder coating, which consequently contributed to better protection of the substrate against moisture, more effective removal of contaminants, and an extended service life of the protected component.

In assessing the anticorrosive properties of the powder coatings, the study of low-temperature powder coatings was extended to include modifications with graphene oxide (GO). [6]. A commercial crosslinking agent, VESTANAT B1358/100, was used, allowing the curing temperature to be set at 160°C for 15 minutes. Using the in situ method, the amount of added graphene oxide (GO) was optimized. The content of GO in the powder coating significantly impacted the final properties of the product. The optimal value chosen was 0.5% by weight of graphene oxide. The presence of this modifier increased the hardness, scratch resistance, formability, contact angle, and resistance to corrosive media of the obtained coatings. However, the coating with the highest GO content (3% by weight) exhibited the lowest flexibility, hydrophobicity, hardness, and showed the lowest corrosion resistance.

In the publication titled "Materials Correlation between the Chemical Structure of (Meth)Acrylic Monomers and the Properties of Powder Clear Coatings Based on Polyacrylate Resins," the focus was on presenting the correlation between the chemical structure of meth/acrylic monomers and the properties of powder coatings based on acrylic resins [7]. In this study, not only were the previously used monomers 2-hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA), and butyl acrylate (BA) employed to create the HEMA:5MMA:2BA resins, but also other acrylates were tested. Instead of 1 mole of BA, the resins included *tert*-butyl acrylate (tBA), dodecyl acrylate (DA), ethyl acrylate (EA), or benzyl acrylate (BAZ). In addition to the final properties of the powder coatings, parameters such as glass transition temperature (T_g) and viscosity had a significant impact. The long hydrocarbon chain attached to the ester group greatly improved flowability and formability but reduced the T_g. A transition glass temperature that was too low led to issues with storing and applying the powder coatings. Therefore, a resin was developed consisting of 1 mole of HEMA, 6 moles of MMA, 0.5 moles of BA, and 0.5 moles of DA. Reducing the content of dodecyl acrylate in the acrylic resin enabled proper application and storage of the powder coating at ambient temperatures. This coating exhibited suitable flowability, the highest contact angle (93.53 degrees), scratch resistance (550 g), formability (13.38 mm), and good impact resistance compared to other samples. Developing a powder coating based on this resin could significantly impact its potential application to components with irregular shapes or sharp edges. The increased flexibility of these coatings can minimize the risk of cracking, ensuring long-term durability.

The article concluding the thematic series on powder coatings based on acrylic resins containing hydroxyl groups focused on the development of self-healing, low-temperature powder coatings [8]. The first step, after characterizing the blocked 1,2,4-triazole polyisocyanate and preparing the appropriate coating composition, involved curing the coating. To initiate the curing process, the deblocking reaction was conducted at temperatures between 110 and 130°C. During curing, the deblocked -NCO groups reacted with the -OH groups from the acrylic resin, resulting in low-temperature powder coatings. During the deblocking reaction, the 1,2,4-triazole reacted with the commercial unsaturated polyester resin. This reaction facilitated the Diels-Alder reaction, leading to the formation of a dien-dienophile adduct. The Diels-Alder and retro-Diels-Alder reactions were confirmed at temperatures of 60-85°C and

90-130°C, respectively, using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and FTIR spectroscopy.

Studies on the Synthesis of Acrylic Resins Containing Epoxyl Functional Groups for Powder Coatings

Research on powder coatings based on acrylic resins containing epoxy functional groups focuses on developing UV-cured coatings. The key monomer facilitating the reaction between the photoinitiator and the resin under UV radiation is glycidyl methacrylate (GMA). Methyl methacrylate and n-butyl acrylate were also used during free radical bulk polymerization, and their molar ratios were optimized accordingly.

The UV curable powder coating described in article titled "UV-Cured Powder Transparent Coatings Based on Oligo(meth)acrylic Resins" [9]. As previously mentioned, glycidyl methacrylate facilitated the cationic photopolymerization reaction with the photoinitiator, hexafluorophosphate triarylsulfonium (2% wt.). Methyl methacrylate, as in previous results, improved the thermal stability, viscosity, and hardness of the resulting coatings. Conversely, n-butyl acrylate enhanced the gloss, flowability, and wetting angle of the powder coatings. The optimal molar ratio of MMA to BA was found to be 6:1. To confirm the advantages of UV curing for powder coatings, wooden panels and MDF boards typically sensitive to high curing temperatures were prepared. These substrates were heated using an IR lamp to remove moisture and to facilitate electrostatic application of the coating on low-conductive materials. Optical microscopy was used to verify that the wood and MDF did not degrade at 130°C and under UV radiation. The images confirmed the absence of surface defects after exposure to 130°C. Additionally, the coatings applied to MDF and wood exhibited good mechanical properties.

The study of the article titled "Preparation and Characterization of Duplex PEO/UV-Curable Powder Coating on AZ91 Magnesium Alloys" can enabled application on the heat sensitive materials as magnesium alloys [10]. The magnesium alloys is challenging due to the instability of magnesium substrates at elevated temperatures. Additionally, ensuring proper adhesion of the organic coating to the magnesium substrate poses a further problem. The acrylic resin containing epoxy groups enabled better adhesion and UV curing. The undercoat was applied through plasma electrolytic oxidation (PEO) in a basic silicate electrolyte. The synthesized coating system was tested using techniques such as scanning electron microscopy (SEM), adhesion to the substrate (by the cross-cut test), and corrosion resistance using Electrochemical Impedance Spectroscopy (EIS). The duplex PEO/UV-curable coating demonstrated very good adhesion to the metal and enhanced protective properties against corrosive media compared to a powder coating applied directly on the magnesium alloy and an alternative conversion coating (synthesized through chemical zirconium phosphating).

An innovation in the development of antimicrobial powder coatings was the use of environmentally friendly biocides, such as chitosan (CH) and chitosan intercalated in montmorillonite (CH/MMT), without the use of silver, which is commonly used in standard antibacterial coating systems. Additionally, acrylic resin containing epoxy groups was employed to enable UV photopolymerization [11]. SEM/EDS analysis revealed that the presence of chitosan causes rupture of microbial cell membranes and leakage of intracellular components. The powder coating's ability to reduce *Escherichia coli* bacteria is significantly stronger compared to *Staphylococcus aureus* (golden staph), likely due to differences in the cell wall structure of these bacteria. Natural antimicrobial modifiers did not significantly affect the mechanical properties of the powder coatings but exhibited beneficial properties such as high scratch resistance and hardness. The use of powder coatings based on acrylic resin containing epoxy groups not only ensured good physicomechanical properties but also expanded the application of the resulting antibacterial powder coatings to substrates sensitive to high temperatures. The development of UV-cured powder coatings that are emission-free and have antimicrobial properties aligns perfectly with modern requirements for final surface properties.

Conclusion

This work describes the impact of selecting and the quantity of appropriate (meth)acrylic monomers on the production of powder coatings based on the acrylic resins, which subsequently determined the preparation of coating compositions, curing processes, properties, and related applications. The described articles align with innovative approaches to using acrylic resins for powder coatings and trends related to the paint and powder coating industry. Low-temperature and UV-cured coating systems based on acrylic resins reduce production costs and enable sustainable development in this industry. Modifying resins to improve flexibility expands the applicability of powder coatings to elements with complex shapes. Additionally, the obtained powder coatings containing acrylic resin meet the requirements for reducing VOC emissions without compromising the performance properties of the final product.

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