MACIEJ UMIŃSKI

ORCID: 0009-0008-9036-4102

Polish Corrosion Society

Radiation-cured coating materials

Wyroby lakierowe utwardzane radiacyjnie

Due to environmental concerns, there is an increasing trend to use more environmentally friendly technologies such as radiation curing and water-based systems instead of traditional solvent-based formulations. The low limit of volatile organic compounds released into the atmosphere and reduced environmental pollution is the main driving force for radiation curing technology, with other benefits including safer maintenance, faster painting process and higher end product performance.

Keywords: radiation curing, water-based radiation curing systems, UV/EB cured coatings, radical mechanism, cationic mechanism, anionic mechanism

Ze względu na ochronę środowiska coraz częściej stosuje się bardziej przyjazne technologie, takie jak utwardzanie radiacyjne i systemy wodorozcieńczalne, zamiast dobrze znanych wyrobów na bazie rozpuszczalników. Niskie limity dotyczące lotnych związków organicznych uwalnianych do atmosfery i dążenie do zmniejszenia negatywnego oddziaływania na środowisko wpływają na rozwijanie technologii utwardzania radiacyjnego. Inne zalety tego rozwiązania to: bezpieczniejsza praca, szybszy proces malowania i wyższa jakość produktu końcowego.

Słowa kluczowe: sieciowanie radiacyjne, wodne systemy sieciowane radiacyjnie, powłoki sieciowane UV/EB, mechanizm utwardzania rodnikowego, mechanizm kationowy, mechanizm anionowy

1. Introduction

Radiation curing of coating materials involves the use of a high-intensity energy source to initiate a chemical reaction resulting in the creation of a high-molecular-weight product from low-molecular-weight raw materials. The energy-initiated polymerization follows a chain mechanism involving the reaction of a generated active center with a monomer. Such a center can be a radical, a cation or, much less frequently, an anion. The energy source is ultraviolet radiation (UV) or electron beam (EB) [1–3]. The curing process itself usually involves radical polymerization or a polyaddition reaction [4–6]. Radical curing technology is considered to be the fastest and most efficient method for converting solvent-free liquid monomers and oligomers into a cross-linked polymer. The cross-linking process takes place at room temperature and, when exposed to radiation, the liquid film of the paint or varnish forms a coating in a very rapid process.

Radiation-cured systems consist of oligomers, prepolymers, mono- and multifunctional monomers, photoinitiators and co-

-initiators (in UV systems) and possibly other substances (pigments, fillers, auxiliary agents such as defoamers, wetting agents, stabilizers, adhesion promoters, inhibitors).
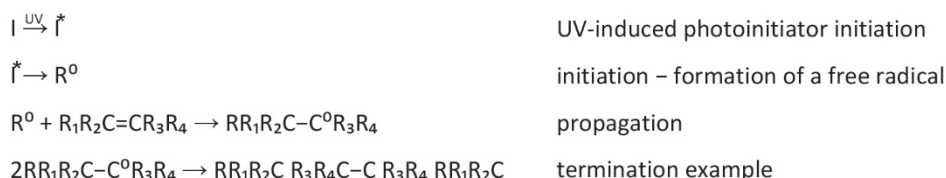
Radiation curing technology started to develop in the 1960s in Germany. Initially, products based on unsaturated polyesters were introduced. The method continues to develop rapidly due to the versatility of its applications and the practical absence of VOC emissions. This latter environmental aspect in particular means that the market for radiation crosslinking materials is increasing by more than 10% each year. The estimated European market for raw materials used in radiation curing technologies is currently around 200,000 tonnes per year. The method is used in solvent-free oligomer and monomer systems [3], water-based coating materials [7], as well as powder coatings [8, 9].

The products obtained by radiation curing are very diverse. These include coating products for wood, metal, plastics, glass, as well as adhesives and printing inks. This method is used to coat automotive equipment and various types of machinery, structural metal components, furniture, flooring, food containers, glass products, buckets and bottles, cosmetic and food packaging, elec-

Dr inż. Maciej Umiński – graduated from the Warsaw University of Technology in 1978 where he studied at the Faculty of Chemistry. In 1982, he earned his doctoral degree in chemical sciences at the same faculty. Between 1992 and 1995, he held a position at Larac SpA (Chemie Linz research center) in Italy, contributing to research and development endeavors focused on core-shell copolymers and radiation curing. He had spent a significant number of years working in the coatings industry. Prior to his retirement in 2021, he worked for Omya sp. z o.o.

Dr inż. Maciej Umiński – w 1978 r. ukończył studia na Wydziale Chemicznym Politechniki Warszawskiej. W 1982 r. uzyskał stopień doktora na tym samym wydziale. W latach 1992–1995 pracował we Włoszech w Larac SpA (ośrodek badawczy Chemie Linz), zajmując się kopolimerami *core-shell* i sieciowaniem radiacyjnym. Przez wiele lat pracował w przemyśle farb i lakierów. W 2021 r. przeszedł na emeryturę z firmy Omya sp. z o.o.

$I \xrightarrow{UV} I^*$ UV-induced photoinitiator initiation

$I^* \rightarrow R^o$ initiation – formation of a free radical

$R^o + R_1R_2C=CR_3R_4 \rightarrow RR_1R_2C-C^oR_3R_4$ propagation

$2RR_1R_2C-C^oR_3R_4 \rightarrow RR_1R_2C\ R_3R_4C-C\ R_3R_4\ RR_1R_2C$ termination example

Scheme 1. UV-curing process

Schemat 1. Proces sieciowania pod wpływem UV

tronic components, compact discs, and the technology in question is used in modern dental fillings [10, 11].

2. Mechanism of polymerization in free radical radiation curing

Free radical radiation curing systems are most commonly used in production practice. The most common UV system requires the use of a photoinitiator, often with a co-initiator, while in EB systems an initiator is not necessary – radicals are formed by decomposition from monomers and oligomers under the influence of a high-energy electron beam. UV systems allow easy and rapid retooling of the process line for the production of further products and are ideal for the manufacture of short product runs. EB systems, on the other hand, are less common due to their high investment cost and their use is limited to high-volume applications [10]. Due to the lack of an initiator, EB formulations are about 5% cheaper than UV formulations. In addition, coatings obtained from EB systems are more homogeneous and more durable due to the fact that they do not have any built-in fragments coming from the photoinitiator.

The earliest industrially applied UV-initiated radical polymerization process is based on the breakdown of a photoinitiator after irradiation with the generation of radicals that react with monomers and oligomers to initiate the formation of the polymer network. The stages involved are: initiation of the initiator, generation of free radicals, propagation and termination (Scheme 1).

In the case of EB systems, a radical is formed under the influence of energy from the monomer or oligomer, which initiates the polymerization reaction. The radical process (UV, EB) is very rapid and polymerization occurs in a fraction of a second. Some problems can include incomplete reaction and the presence of small amounts of unreacted monomers, which can reduce the durability of the coating.

3. Raw materials used in free radical radiation curing

Monomers, oligomers and prepolymers are used as polymerizable reactants. Monofunctional monomers, often referred to as reactive diluents, act as viscosity regulators and affect the adhesion and shrinkage of the finished coating. Multifunctional monomers form a polymer network, improving the hardness and other mechanical parameters of the coating. Oligomers and prepolymers of relatively low molecular weight, containing a polymerizable acrylic residue, are responsible for most of the mechanical parameters and chemical resistance of the finished coating. The prepared formulation must have an adequate working viscosity, which is not easy to achieve, especially with linear oligomers. The solution is to use hyperbranched monomers and prepolymers, which have a much lower viscosity [12–14], thus eliminating or reducing the amount of

reactive solvents in the formulation (which also solves the problem of toxicity) and avoiding the use of organic solvents (thus eliminating the problem of VOC emissions).

Various types of acrylates, styrene, unsaturated polyesters and mixtures of maleates with vinyl ethers are used most often. Acrylic derivatives are still the most important.

The simple mono-, di- and triesters of acrylic and methacrylic acid were used as raw materials, especially in the early days of the technology's development. To date, 2-ethylhexyl acrylate (EHA), 1,6-hexanediol diacrylate (HDDA), tripropylene glycol diacrylate (TPGDA), trimethylolpropane triacrylate (TMPTA), pentaerythritol triacrylate (PETA) and trimethylolpropane trimethacrylate (TMPTMA) are used. Mono- and diacrylates are excellent at reducing system viscosity and providing good adhesion; their conversion rate in the cross-linked formulation is moderate to high. Due to their high volatility and reactivity, their toxicity is mostly high. Triacrylates, on the other hand, cure quickly but have poor adhesion, high shrinkage and form a brittle film; their toxicity is moderate.

So-called second-generation monomers are acrylic esters of ethoxylated and propoxylated glycols [15]. These substances react quickly, the shrinkage is much lower and, very importantly, their toxicity is markedly lower. Examples include propoxylated neopentyl glycol diacrylate (NPG(PO)DA) or trimethylolpropane ethoxylate triacrylate (TMP(EO)TA).

The third generation group of monomers includes various types of raw materials. They show low viscosity and shrinkage, high oligomer solubility and their toxicity is very low [15]. Examples include methoxyacrylates, often ethoxylated or propoxylated, and acrylate molecules having an incorporated cyclic carbonate, carbamate or oxazolidine group. Another group of useful monomers includes 3-oxy-bis methacrylates, characterised by a very high conversion rate and very low shrinkage, as well as oligomeric acrylate derivatives of hexamethoxymethylmelamine, which can be cross-linked both by a free radical process (due to the presence of acrylate groups) and by a condensation mechanism (owing to the content of methoxyl groups).

4. Advantages and disadvantages of the classic radiation curing process

The problem with solvent-free UV systems is the need to achieve adequate working viscosity, which requires the addition of a reactive solvent (monomer), which has some toxicity and is potentially irritating and sensitizing [16]. Available literature data often vary, the Primary Skin Irritation Index (PII) values given cannot therefore be considered as absolute values, but certain trends are apparent and it is possible to predict the harmfulness of individual

monomers quite accurately. For example, low-viscosity acrylic monomers are more toxic than monomers with slightly higher viscosity. It has also been found that ethoxylation or propoxylation of the starting alcohols reduces the viscosity of the resulting acrylic esters and simultaneously reduces the PII value. The use of alkoxylated alcohols for esterification also reduces shrinkage during polymerization, which increases the durability of the resulting coating.

Free-radical radiation curing is superior to traditional technologies in many respects, but it also has some disadvantages, which have been significantly reduced as research has developed (Table 1).

Table 1. Advantages and disadvantages of using a free radical radiation curing process
Tabela 1. Zalety i wady stosowania wolnorodnikowego procesu utwardzania radiacyjnego

Advantages	Disadvantages
Environmentally friendly process, no solvents (0% VOCs)	Possible risk due to some toxicity of acrylic monomers
High yield due to very short polymerization time	Initial limitations in coating thickness and pigmentation in UV process
Saves energy and production space	Moderate adhesion to substrate for typical acrylic formulations – problem solved by using suitable monomers
Coating can be applied to heat-sensitive substrates	Higher viscosity of coating material hinders application – problem solved by using suitable monomers
Highly cross-linked structure allows high gloss and excellent mechanical and chemical properties of the coating	Coating shrinkage and incomplete polymerization of the system was an initial problem
No production waste	Higher raw material and line maintenance costs
Total method cost comparable to solvent technology and yet no environmental problems	Difficulty in removing the coating from the substrate can make recycling difficult
High quality of the resulting coating	In the UV method, initially problems with curing coatings on 3D objects

Most of the disadvantages described in Table 1 have been eliminated or clearly reduced. The use of appropriately selected and surface-treated pigments allows UV coatings to be prepared in as full a color range as possible [17], for example, the initial problem of using titanium white was solved by surface treatment of titanium dioxide, improving UV transmittance, as well as by selecting an appropriate photoinitiator system and radiation sources. Toxicity and shrinkage phenomena, as well as problems in achieving optimum working viscosity, were reduced by appropriate selection of monomers and oligomers in the formulation. The use of efficient lamps with a narrow UV emission band and a suitable UV mirror system enabled faster and complete curing of the coating on complex-shaped objects while reducing substrate heating. A drawback of the method is the negative effect of oxygen on free radical polymerization. Working in inert atmospheres (nitrogen or argon) is no longer necessary due to the correct choice of energy sources [18] and monomers and the use of more active photoinitiators [19, 20]. Modern coating compositions based on acrylic resins containing disulphide groups have the ability to self-heal a damaged coating and also show excellent anti-corrosion properties [21, 22].

5. Water-based radiation curing systems

An interesting alternative to solvent-free UV systems may in some cases be the technology of water-based radiation-cured products. It combines the advantages of water-based products and traditional radiation curing systems. A stable aqueous dispersion of macromers, when applied to the substrate and exposed to energy (UV, EB), forms a coating [7, 23, 24]. The system described is particularly suitable for coating porous surfaces such as paper, wood, plasterboard or concrete. The water contained in the applied paint soaks quickly into the porous substrate and the coating is almost immediately ready for cross-linking. When applying a thick layer of coating material, an additional pre-drying step is required before the radiation cross-linking step. The great advantage of water-based UV technology is that it is not necessary to use reactive thinners, which are a source of health risks (they are often toxic and have an allergenic effect) in classical UV technology. Other advantages of this method include: easy cleaning of the installation and equipment, the possibility to apply the coating by spray or roller, easy achievement of working viscosity and lower cost [25]. Table 2 summarizes the advantages and disadvantages of using UV-curable water-based paint products.

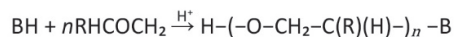**Table 2. Advantages and disadvantages of using water-based UV-curing coatings**
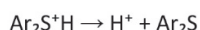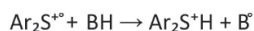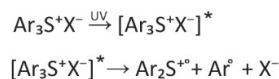**Tabela 2. Zalety i wady stosowania wodorozcieńczalnych wyrobów lakierowych utwardzanych za pomocą UV**

Advantages	Disadvantages
No reactive solvents: reduced toxicity, flammability and odor intensity; lower cost than standard UV solvent-free technology; minimal coating shrinkage, better adhesion	Use of water as a diluent: low-porosity substrates require a drying step before the curing step if a thick layer is applied; wetting problems – the solution is to add wetting agents
Low formulation viscosity, easy control of system rheology: curtain, spray and roller application possible	Slower production process than with standard UV technology
Higher gloss level than physically drying water-based products	Sometimes lower gloss level than with standard UV technology
Easy cleaning of the production line	For some surfaces, poorer adhesion and lower durability of the coating

When applying the coating to polar substrates, the addition of macromonomers containing maleate groups with double bonds capable of copolymerization with other acrylic monomers and oligomers can be used [26]. Water-based radiation curing systems are developing even faster than classical UV technology.

6. The mechanism and raw materials used in the cationic radiation curing process

One limitation of the free radical process is its sensitivity to oxygen in the atmosphere [19]. While this effect can be minimized by the use of hyperbranched urethaneacrylates [14], a better way is to use a crosslinking mechanism that is insensitive to the presence of oxygen. Such a solution is the cationic mechanism, which is increasingly used in industry for complex applications, for example to obtain organic-inorganic hybrid coatings [27]. Cationic systems are based on the proton-catalyzed polyaddition reaction of vinyl ethers, styrene, N-vinylcarbazole, epoxides, cyclic ethers, lactones and
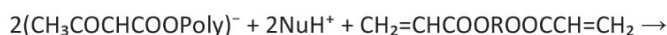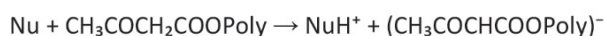
$$Ar_3S^+X^- \xrightarrow{UV} [Ar_3S^+X^-]^*$$

$$[Ar_3S^+X^-]^* \rightarrow Ar_2S^{+\circ} + Ar^\circ + X^-$$

$$Ar_2S^{+\circ} + BH \rightarrow Ar_2S^+H + B^\circ$$

$$Ar_2S^+H \rightarrow H^+ + Ar_2S$$

$$BH + nRHCOCH_2 \xrightarrow{H^+} H-(-O-CH_2-C(R)(H)-)_n -B$$

Ar – aryl

BH – proton donor

X – BF_4, PF_6, SbF_6, AsF_6

Scheme 2. UV-induced cationic polymerization process
Schemat 2. Proces polimeryzacji kationowej pod wpływem UV

$$ZNu \xrightarrow{UV} Z + Nu \qquad \text{UV-induced formation of a nucleophilic base/molecule}$$

$$Nu + CH_3COCH_2COOPoly \rightarrow NuH^+ + (CH_3COCHCOOPoly)^-$$

$$2(CH_3COCHCOOPoly)^- + 2NuH^+ + CH_2=CHCOOROOCCH=CH_2 \rightarrow$$

$$\rightarrow PolyOCOCH(COCH_3)CH_2CH_2COOROOCCH_2CH_2(COCH_3)CHCOOPoly + 2Nu$$

Poly – polymer chain

R – alkyl residue

Scheme 3. Example of Michael reaction
Schemat 3. Przykładowa reakcja Michaela

cyclic acetals [7, 28]. The catalysts consist of sulfonium or iodonium salts. UV radiation produces molecules of strong Brønsted acids, which migrate through the applied layer of the coating product, catalyzing the polyaddition reaction [29, 30] (Scheme 2). It can be assumed that the share of cationic systems in the European market for radiation curing systems currently accounts for almost 10%.

The cationic curing mechanism is not sensitive to the presence of oxygen (no air inhibition occurs), but is slowed down or even completely inhibited by nucleophilic substances that bind protons catalyzing the polymerization reaction. The monomer polyaddition reaction proceeds rapidly and the resulting coating exhibits virtually no shrinkage and excellent adhesion to the substrate, which is difficult to achieve with a free radical process. Industrially, epoxides and vinyl ethers have the greatest relevance and can be an alternative to acrylates in the free radical process due to their low toxicity, low odor and high reactivity. The so-called dark curing, or post-curing effect, allows the reaction to proceed even in underexposed and post-exposure areas [31]. This has a particularly strong significance for complex surfaces in three-dimensional objects. To reduce the brittleness of the resulting epoxy polymers, improve impact resistance and reduce crack propagation, core-shell copolymers containing a soft core and a shell with reactive epoxy groups can be used [31].

Table 3. Advantages and disadvantages of using cationic UV-curing systems
Tabela 3. Zalety i wady stosowania kationowych systemów utwardzanych pod wpływem UV

Advantages	Disadvantages
Oxygen does not inhibit the polymerization reaction, it is not necessary to work in an inert atmosphere	Nucleophilic substances inhibit the process – need to eliminate them from the formulation
Relatively fast process, after UV irradiation the reaction proceeds to completion	Slightly slower process than standard UV-crosslinking
Virtually no shrinkage, very good adhesion to the substrate, better mechanical properties of the coating than with the standard UV method	Higher formulation cost compared to standard UV method
Can be used for complex 3D objects, even incomplete irradiation results in virtually complete conversion	For some epoxies, the resulting coating is brittle; the solution is to add fillers and thermoplastic polymers, for example core-shell polymers
Very low toxicity of the raw materials used	×

7. Cross-linking by the anionic mechanism

Another possibility is the use of an anionic mechanism, involving the UV-induced generation of a nucleophilic substance capable of initiating the polymerization process. Such a reaction could be, for example, the well-known Michael reaction, involving the attachment of an enolate anion to the carbon-carbon bond of α,β-unsaturated derivatives of carboxylic acids, nitriles, ketones or aldehydes. The base (a strong nucleophile) producing the enolate anion is the catalyst that reproduces itself in the condensation process [32].

A strong nucleophile such as tetramethylguanidine (TMG), which has a pKa of 13.6, is a very efficient catalyst for the Michael reaction, which can be catalyzed by active monomers and oligomers containing acidic hydrogen atoms bonded to a carbon atom [33]. Acrylic acetylacetate derivatives containing an active methylene group may constitute such substances [34] (Scheme 3).

A photolatent TMG precursor that produces free tetramethylguanidine under UV exposure has been described in the literature [35]. A UV system using a photolatent catalyst precursor has also been developed, producing upon irradiation tertiary amines that are weaker bases than TMG and cross-link a system of two polymers containing a functional SH group and an isocyanate group [36, 37].

8. Further developments in radiation curing technology

In addition to the introduction of new monomers, oligomers, catalysts [38–41] and more efficient energy sources [42, 43], there is promising work on hybrid systems that crosslink by different mechanisms [27, 33, 39, 44, 45], and on UV powder coatings [9]. Systems cured by the anionic mechanism are expected to develop rapidly.

Research on radiation curing systems containing structural organic-inorganic copolymers that modify the final mechanical and physicochemical parameters of the resulting coating will be very important. In this way, it will be possible to introduce core-shell structures with a core that is a pigment molecule, a functional filler, including metallic or anticorrosive fillers, or a catalyst [46]. Such core-shell composites allow homogeneous dispersion of inorganic particles in the formulation, which, in addition to a more efficient use of the pigment or filler, should result in easier UV penetration

into the liquid coating and a higher conversion degree of double bonds of monomers and oligomers.

BIBLIOGRAPHY

[1] J. P. Fouassier, J. F. Rabek (eds.). 1993. *Radiation Curing in Polymer Science and Technology*. Vol. 1: *Fundamentals and Methods*. London: Elsevier.

[2] D. R. Bloch. 1994. "Acrylic Monomers for Radiation-Cured Adhesives and Coatings." *Adhesive Age* 37(4): 30–34.

[3] M. Umiński, L. M. Saija. 1995. "Acrylic Monomers for Radiation Curing." *Surface Coatings International* 78(6): 244–249.

[4] M. Umiński. 1999. „Farby i lakiery przyjazne środowisku". *Rynek Chemiczny* 2: 22–23.

[5] M. Umiński. 2008. „Nowe technologie w zdobieniu wiader i innych opakowań w firmie Plast-Box S.A.". *Opakowanie* 53(1): 48–49.

[6] C. Decker. 1987. "UV-Curing Chemistry: Past, Present, and Future." *Journal of Coatings Technology* 59(751): 97–106.

[7] M. Umiński. 1997. "Waterborne UV/EB Curing Systems." *Pigment and Resin Technology* 26(3): 149–152. DOI: 10.1108/03699429710168708.

[8] M. Müller. 2004. "A Professional Life with UV Manfred Müller on Milestones of Success in Radiation Curing." *European Coatings Journal* 5: 18.

[9] M. Manea, K. Ogemark, L. S. Svensson. 2005. "Network Controllers: Using Crosslinkers to Tailor Properties of UV Powder Coatings." *European Coatings Journal* 12: 26–30.

[10] IAL Consultants Ltd. 1990. *An Overview of the European Radiation Curing Market*. London.

[11] D. Skinner. 2009. "Making Light Work for a Living: Innovations Drive Market Growth in UV/EB Applications across Europe." *European Coatings Journal* 10: 18–20.

[12] Y. Chen, N. Wang, G. Tong, D. Wu, X. Jin, X. Zhu. 2018. "Synthesis of Multiarm Star Polymer Based on Hyperbranched Polyester Core and Poly(ε-caprolactone) Arms and Its Application in UV-Curable Coating." *ACS Omega* 3(10): 13928–13934. DOI: 10.1021/ACSOMEGA.8B02128.

[13] E. Langer, M. Zubielewicz, G. Kamińska-Bach, S. Jurczyk, T. Bańcer, A. Ziółkowski. 2023. „Innowacyjne bezołowiowe farby utwardzane promieniami UV do malowania szkła użytkowego". *Ochrona przed Korozją* 66(9): 274–287. DOI: 10.15199/40.2023.9.1.

[14] B. Dunjić, S. Tasić, B. Božić. 2004. "Hyperbranched Urethane-Acrylates." *European Coatings Journal* 6: 36–41.

[15] R. Mullin. 1992. "Spotlight on Radiation Curing: Formulating for New Applications." *Chemical Week* 5: 22–26.

[16] P. Megens. 1994. "Low Viscous UV-Curable Wood Coatings." *Surface Coatings International* 77: 245–249.

[17] J. P. Fouassier, L. Simonin-Catilaz. 1995. "UV Drying: The First Industrial One-Step Process." *European Coatings Journal* 4: 272–276.

[18] K. Efsen. 1994. "Radiation Curing Equipment". *Surface Coatings International* 77: 234–242.

[19] C. Decker, K. Moussa. 1993. "Recent Advances in UV-Curing Chemistry." *Journal of Coatings Technology* 65(819): 49–57.

[20] C. Decker, K. Moussa. 1990. "A New Class of Highly Reactive Acrylics Monomers, 1: Light-Induced Polymerization." *Die Makromolekulare Chemie, Rapid Communications* 11(4): 159–167. DOI: 10.1002/marc.1990.030110404.

[21] D. Zhao, S. Liu, Y. Wu, T. Guan, N. Sun, B. Ren. 2019. "Self-Healing UV Light-Curable Resins Containing Disulfide Group: Synthesis and Application in UV Coatings." *Progress in Organic Coatings* 133: 289–298. DOI: 10.1016/j.porgcoat.2019.04.060.

[22] T. Li, Z. P. Zhang, M. Z. Rong, M. Q. Zhang. 2019. "Self-Healable and Thiol-Ene UV-Curable Waterborne Polyurethane for Anticorrosion Coating." *Journal of Applied Polymer Science* 136(26): 47700. DOI: 10.1002/app.47700.

[23] C. Decker, F. Masson, R. Schwalm. 2004. "How to Speed up the UV Curing of Water-Based Acrylic Coatings." *Journal of Coatings Technology and Research* 1(2): 127–136. DOI: 10.1007/s11998-004-0007-1.

[24] S. Mamat, L. C. Abdullah, M. M. Aung, S. A. Rashid, M. Z. Salleh, S. Saalah, E. R. Jusoh, M. Rayung. 2023. "Synthesis and Characterization UV-Curable Waterborne Polyurethane Acrylate/Al_2O_3 Nanocomposite Coatings Derived from Jatropha Oil Polyol." *Biointerface Research in Applied Chemistry* 13(2): 193. DOI: 10.33263/briac132.193.

[25] O. Valdes-Aguilera, A. Carmack, M. de Lombard-Watts. 2007. "UV-Curable Polyurethane Acrylate Dispersions Compared to 100% Solids UV-Curable Urethane Acrylates." *Paint and Coatings Industry* 23(4): 36–42.

[26] L. M. Saija, M. Umiński. 1995. "Unsaturated Alcohols and Glycols Containing Ionizable Groups for Synthesis of Urethane Acrylate Graft Copolymer Latices." *Die Angewandte Makromolekulare Chemie* 233(4069): 103–112. DOI: 10.1002/apmc.1995.052330109.

[27] C. Croutxé-Barghorn, A. Chemtob, C. Belon. 2009. "Parallel Processing: Photocuring Combines Epoxy and Sol-Gel Reactions in a Single Step." *European Coatings Journal* 10: 24–27.

[28] J. P. Fouassier. 1994. "New Developments in Photoinitiators and Photosensitizers for Conventional and Laser Curing of Multifunctional Organic Materials." *Surface Coatings International* 6: 252–258.

[29] S. P. Pappas, J. H. Jilek. 1979. "Photoinitiated Cationic Polymerization by Photosensitization of Onium Salts." *Photographic Science and Engineering* 23(3): 40–143.

[30] J. V. Crivello. 2007. "Synergistic Effects in Hybrid Free Radical/Cationic Photopolymerizations." *Journal of Polymer Science: Part A: Polymer Chemistry* 45: 3759–3769. DOI: 10.1002/pola.22126.

[31] M. Sangermano, N. Razza, J. V. Crivello. 2014. "Cationic UV-Curing: Technology and Applications." *Macromolecular Materials and Engineering* 299(7): 775–793. DOI: 10.1002/mame.201300349.

[32] H. O. House. 1979. *Nowoczesne reakcje syntezy organicznej*. Warszawa: PWN.

[33] M. Umiński. 2007. "Environment-Friendly Polymeric Binders." *Paint and Coatings Industry* 23(8): 38–43.

[34] F. D. Rector, W. W. Blount, D. R. Leonard. 1989. "Applications for Acetoacetyl Chemistry in Thermoset Coatings." *Journal of Coatings Technology* 61(771): 31–37.

[35] W. A. D. Stanssens, J. F. G. A. Jansen. 1998. *Anionic Photocatalyst*. US Patent 6124371.

[36] K. Dietliker, K. Misteli, T. Jung, P. Contich, J. Benkhoff, E. Sitzmann. 2005. "Novel Chemistry for UV Coatings: Photolatent Base System Optimises Performance for Refinish Clearcoats." *European Coatings Journal* 10: 20–24.

[37] N. Dogan, H. Klinkenberg, L. Reinerie, D. Ruigrok, P. Wijnands. 2005. "Finishing in the Fast Lane: Thiol-Isocyanate UV System Speeds up Automotive Repair Coating." *European Coatings Journal* 11: 36–40.

[38] M. Visconti, M. Cattaneo. 2004. "Difunctional Photoinitiators Can Solve Migration and Odour Problems in Clearcoats and Pigmented Systems." *European Coatings Journal* 5: 20–24.

[39] C. Decker. 2005. "Linked by Light: Advances in the UV-Curing of Organic Coatings." *European Coatings Journal* 7–8: 28–32.

[40] A. Fonzé, D. Heymans, N. Henry, H. Hendrickx. 2006. "Versatile Versatate: Acrylate Esters of Glicidyl Versatate Can Outperform Conventional Monomers in UV Curing Laminating and Pressure-Sensitive Adhesives." *European Coatings Journal* 1–2: 42–45.

[41] M. Tielemans, J. P. Bleus, M. Vasconi. 2007. "Braving the Weather: A New UV-Curable Polyurethane Dispersion for Outdoor Applications on Wood." *European Coatings Journal* 3: 38–42.

[42] T. Molamphy. 2007. "Curing in a New Light: Next Generation Solid State Array UV Light Sources Outperform Conventional Arc Lamps." *European Coatings Journal* 2: 38–40.

[43] T. Jung, P. Simmendinger, W. Tobisch. 2005. "Out of the Shadows: Plasma Process Facilitates UV Curing in Three Dimensions." *European Coatings Journal* 4: 138–143.

[44] C. Vu, O. Laferté. 2006. "All Layers Count: Silica Nanoparticles in the Optimisation of Scratch and Abrasion Resistance of High Performance UV Multi-Layer Coatings." *European Coatings Journal* 6: 34–38.

[45] M. Umiński. 2023. "Core-Shell Copolymers and Hybrid Composites as Valuable Raw Materials for Industrial Coatings." https://digitaledition.pcimag.com/november-2023/feature-uminski/https://digitaledition.pcimag.com/november-2023/feature-uminski/ (access: 20.11.2023).

[46] M. Umiński. 2023. „Organiczne i organiczno-nieorganiczne polimery *core-shell* jako wartościowe surowce do wodorozcieńczalnych wyrobów antykorozyjnych". *Ochrona przed Korozją* 66(9): 295–297. DOI: 10.15199/40.2023.9.3.